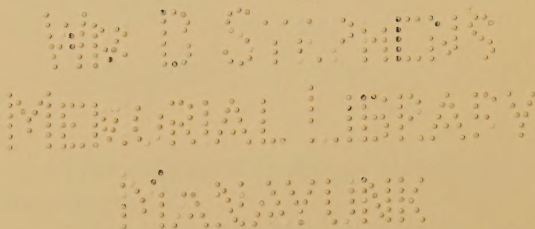# INTERMEDIATES FOR DYESTUFFS

INTERMEDIATES FOR DYESTUFFS

BY

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INTRODUCTION

What are the causes of the colour and the dyeing properties of a dyestuff? This is a twofold question. Colour and dyeing power are separate and distinct qualities. A dyestuff may be so fixed on or in the fibres of the material to be dyed that it cannot be immediately washed off. Not all coloured substances possess this property. On the other hand, there are colourless substances, such as tannic acid, β-hydroxynaphthoic anilide, hydrated alumina, etc., which can be fixed, in the sense just mentioned, on cotton, wool, and other textile materials.

As regards the cause of the colour in a dyestuff, the preliminary generalisation can be made—though it does not carry us very far—that the known dyestuffs are complex organic compounds containing—

(a) The ringed nuclei of benzene, naphthalene, anthracene, and certain related ring structures, such as those of carbazole, acenaphthene, indole, etc.

(b) Connecting atoms, or chains of atoms, of carbon, oxygen, nitrogen, and sulphur.

(c) Substituent groups attached to the rings, of which the most prominent are the amino, hydroxyl, sulphonic acid, and nitro groups.

Compounds are, however, known which fulfil all these conditions and yet are colourless. A theory proposed by O. N. Witt proceeds a stage further, and attributes colour, or a predisposition to colour, to the presence of certain " chromophoric " groups—e.g.,

$$>C=O \quad , \qquad >C=N- \quad , \qquad -N=N- \quad , \qquad -NO_2 \quad ,$$

or the more complete groupings,
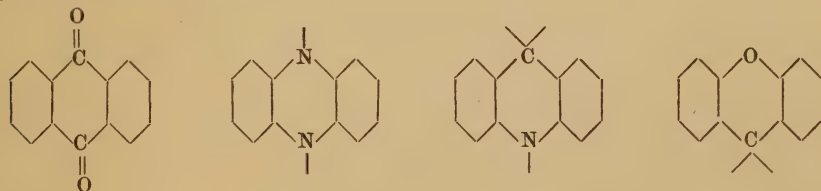
Another view is that proposed by H. E. Armstrong and A. G. Green, according to which quinonoid arrangements in the carbon rings—

p-Quinonoid.　　　　　　o-Quinonoid.

—are responsible for the colour. The two views are not mutually exclusive, but are, indeed, to some extent complementary.

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Dyeing properties—the possession of affinity for the textile fibres—are to be attributed, according to the second part of Witt's theory, to the presence in the molecule (together with the chromophores) of the hydroxyl and amino (or substituted amino) groups. These groups not only impart affinity for the fibre, but also intensify the colour of the substance, and are hence called "auxochromes."

These generalisations are sufficiently in accord with experience to serve as useful guides in the mazes of dyestuff chemistry, and are, in fact, the working hypotheses of the dyestuff chemist. They indicate that the making of dyestuffs involves the following conditions :

(*a*) The **fundamental substances**—the raw materials—are the so-called " aromatic " compounds, benzene, naphthalene, anthracene, and the related toluene, xylenes, phenol, cresols, carbazole, acenaphthene, and so on. The sole economic source of these substances at present is coal tar,* which therefore forms the starting-point for the manufacture of dyestuffs. The isolation of the above-named substances from coal tar is not described in this book. Except in a few cases, it will be assumed that they are available in a sufficiently pure condition for subsequent operations.

(*b*) The **Intermediates.** The raw materials must be so acted on, by various reagents, as to introduce into them the required chromophoric and auxochromic groups, or groups which may in the final stages be convertible into chromophoric and auxochromic groups. Thus, for instance, benzene is nitrated to form nitro-benzene, and this reduced to aniline; naphthalene is sulphonated, and the sulphonic acid converted into a naphthol; anthracene is oxidised to anthraquinone, and so on. None of these products is a dyestuff, but all are capable of immediate conversion to dyestuffs by further operations. They form the intermediates for the dyestuffs, and it is with the processes used in making these intermediates that the following chapters are concerned.

(*c*) The **dyestuffs** are formed in general by the condensation together of two or more intermediates. These final stages are treated in detail in works on the chemistry of the dyestuffs, and will not be dealt with here.

In the preparation of both the intermediates and the dyestuffs, certain non-aromatic substances (apart from the inorganic reagents—the acids, alkalies, etc.) are employed. Thus, formaldehyde and phosgene are used for condensations with amines; methyl and ethyl alcohols, chlorides and sulphates for the alkylation of amino and hydroxyl groups; acetic acid and anhydride for the acetylation of amino groups; acetoacetic ester and oxalacetic ester for condensation with hydrazines to form pyrazolones, and so on. These non-aromatic substances are therefore also, in a sense, intermediates for dyestuffs, but they are, perhaps, more properly to be considered as auxiliaries than as intermediates, and for the purposes of this book they will be so treated.†

No definite and general line of demarcation exists between the intermediates and the dyestuffs. A substance may at the same time be a dyestuff and an intermediate

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* This is sufficient justification for the common name of " Coal Tar Colours " given to the artificial dyestuffs, though the use of this name has given rise, in the minds of the uninstructed, to the idea that these dyestuffs are *extracted* from coal tar.

† A useful summary of the methods of making these auxiliary substances will be found in a paper by J. T. Hewitt (*Journ. Soc. Dy. Col.* 1920, p. 6).

for other dyestuffs. A separate treatment of the intermediates is necessitated rather by convenience due to the wide scope of the subject than by any strictly logical difference between them and the dyestuffs. Such standard works on the chemistry of the dyes as those of Georgievics, Bucherer, and Cain and Thorpe contain chapters dealing with the intermediates, but the information given there is highly condensed and summarised, and the main treatment is reserved for the dyestuffs themselves. The present book may be considered as, in effect, an elaboration of these summaries. This elaboration has not been carried to the fullest possible extent. That would be impossible in a single volume of reasonable size. The number of intermediates listed in the " Colour Index," published by the Society of Dyers and Colourists, amounts to about five hundred, and this includes only those which enter into the composition of commercial dyestuffs of known constitution. A selection has therefore been necessary, and this has been made so as to include most of the important intermediates.

Arrangement of the Material.

The method to be adopted of arranging the matter in a book of this kind presents some difficulty. The various items, large in number and disconnected in nature, might be classified from the systematic chemical point of view as nitro compounds, amines, phenols, sulphonic acids, and the like. But this method has the great disadvantage of separating, perhaps widely, substances which are naturally closely related. The preparation, for example, of 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) is carried out in four stages, which involve the production in turn of a naphthalenetrisulphonic acid, a nitronaphthalenetrisulphonic acid, an aminonaphthalenetrisulphonic acid, and finally the aminonaphtholdisulphonic acid. Under the scheme here suggested, these four stages would be dealt with in widely separated parts of the book. A further difficulty under this scheme is caused by the fact that many of the substances contain several of the substituent groups which form the basis of classification. Whether, for instance, an aminophenol should be classed with the amines or with the phenols is a point for whose decision there is no guiding principle.

Another possible classification is based on the nature of the operations used in the formation of the intermediates from the starting materials—namely, halogenation, nitration, reduction, sulphonation, alkali fusion, and so on. This method is attractive to the chemist who is investigating the preparation of new substances or attempting to improve on the existing methods of preparation of known substances, since, on this plan, the many different modifications of a reaction, such as nitration, are presented together, and are readily available for comparison. The chapters on the intermediates in Bucherer's " Lehrbuch der Farbenchemie " are written from this point of view, and form a valuable summary of the subject. However, the method suffers from the same defect as the preceding one—namely, that the different stages in the preparation of many of the intermediates are necessarily dealt with in widely separated parts of the book.

The classification actually adopted in the succeeding chapters of this book is one which traces the formation of each intermediate, stage by stage, from the coal tar

product which forms its starting material. The various chapters are therefore taken up with the preparation of the intermediates actually made from each coal tar product. The charts at the beginnings of the chapters indicate, it is hoped with sufficient clearness, the number and nature of the stages required for the preparation of a given intermediate, and the treatment in the text follows as closely as possible the order shown in the charts. Complications of order are, of course, caused by branched chains in this genealogical arrangement, and changes of order are made where these seem desirable for the sake of treating together closely connected subjects. The plan has the advantage of showing in brief how, and by how many operations a given intermediate is derived* from the raw material. It does not, however, altogether escape the defect urged against the plans previously discussed, that of separating closely connected subjects. Where, for example, a particular intermediate is obtainable from different sources, or by different methods from the same source, the preparation of that intermediate will be found in several places depending on the source or the method to be described. This defect is remedied by the use of cross references.

Method of Treatment.

The efficient manufacture of a substance involves the solution of complex problems, some of which are of a high order of difficulty. The nature of these problems may be briefly indicated here. They are concerned with the determination of data of all kinds bearing on the nature of the materials and the reactions connected with the preparation of the required substance.

(a) The physical constants of the pure substance must be accurately determined —viz., its crystalline form, melting-point, boiling-point under different pressures, vapour pressure and density over a range of temperature, and so on.

(b) The chemical reactions involved in the process to be adopted are examined, any possible side reactions detected, and the means of preventing or limiting these worked out.

(c) A series of physico-chemical investigations may be required, dealing with the various factors concerned in the process, such as velocities of reaction at different temperatures, and the vapour pressure and solubility curves for the systems composed of the starting materials, solvent, and reaction products.

(d) The most suitable materials for the construction of the plant required must be considered.

All the information gathered along these lines is required for the devising of a manufacturing process of maximum efficiency, and a full account of each of the intermediates dealt with in this book would require all these details. Needless to say, that programme has not been carried out here. In fact, such a minutely detailed study has been worked out for only a comparative few of the dyestuff intermediates, and a description of each of these would require a volume to itself. Admirable models of the kind of thing referred to are to be found in some of the " Technical Records

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* Incidentally, it may be remarked that the word " derivative " is used in this book in a practical sense and not with its systematic chemical meaning.

of Explosives Supply " published by the late Ministry of Munitions. But all that is possible in such a book as the present, which deals with the preparation of several hundreds of substances, is to give a summary of the more important literature connected with each substance, together with references to the sources of more detailed information where such exist. Details of chemical plant and manufacturing technique have been omitted, not because they are unimportant, but because the inclusion of such matter was felt to be unnecessary. The nature of the plant required for any ordinary chemical operation is familiar to the experienced works chemist, and is described in books on chemical engineering.

Applications of the Intermediates.

No description of a dyestuff intermediate would be complete without some reference to the nature of the dyestuffs for which it is used. To give a list of the dyestuffs made from each intermediate, especially if these were referred to under their trade names, would be of little use. In any case, this has already been done in the " Colour Index " previously mentioned. It was considered preferable in this book to attempt to indicate in general terms the class or classes of dyestuffs for which each intermediate is employed, and to estimate the part played by the intermediate in each class, including its influence on the shade, fastness, and other dyeing properties.* These notes on the applications of the intermediates are necessarily brief, since it would hardly be appropriate here to enter into details of the methods of synthesis of the dyestuffs. But it is hoped that these notes, which, taken together, constitute a treatment of the chemistry of the dyestuffs from an unusual point of view, will be found useful and suggestive.

A. D.

November, 1925.

* Further information on the nature of the dyestuffs (and also of many other classes of products) made from these intermediates can be found in " The Industrial Applications of the Coal Tar Products," by H. M. Bunbury and A. Davidson (Ernest Benn, Ltd., 42s.).

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INTERMEDIATES FOR DYESTUFFS

CHAPTER I

THE CHLOROBENZENES AND THEIR DERIVATIVES

A. The Chlorobenzenes.

THE chlorobenzenes of technical importance are :

Monochlorobenzene, C_6H_5Cl, a colourless liquid, b.p. 132°, $D_{4°}^{20°}$ 1·1060.

p-**Dichlorobenzene,** $C_6H_4Cl_2$, a colourless crystalline solid, m.p. 53°, b.p. 174°; soluble in alcohol.

o-**Dichlorobenzene,** a liquid, b.p. 179°.

They are prepared by the action of chlorine gas on benzene, in presence of a catalyst. Chlorine acts very slowly on benzene even at the boil, but the reaction is accelerated by iron, iodine, aluminium, and its chloride, antimony pentachloride, etc. Substitution takes place, and mixtures of monochloro- and dichlorobenzenes are formed together with higher substitution products, the composition of the mixture depending chiefly on the temperature, but also on the catalyst used and on the presence or absence of moisture. As regards the effect of moisture, it has been found that if this is rigidly excluded only addition products are formed. Thus apparently water acts as a chlorine-carrier, and it has been suggested that the source of active chlorine is HOCl. However, the presence of much moisture causes other complications, and if mono- or dichlorobenzenes are required, the chlorination must be carried out in approximately dry conditions.

Among the catalysts, iron is the most important, and is the one used on the manufacturing scale, wrought-iron being preferred to cast-iron, as it acts less vigorously than the latter. Aluminium also acts well, a yield of 87 per cent. of monochlorobenzene having been obtained, using only 1 part of aluminium to 1,000 parts of benzene (Meunier, *C.R.*, 1920, **170**, 1451).

A study of the kinetics of the chlorination of benzene in presence of iron as catalyst has shown that the proportion of monochlorobenzene in the chlorination products rises with the temperature, and at the boiling-point of benzene amounts to about 85 per cent. Again, the molecular proportion of benzene converted to monochlorobenzene in a given time is 8·5 times the molecular proportion of monochlorobenzene converted to dichlorobenzenes in the same time (Bourrion, *C.R.*, 1920, **170**, 1309).

The conditions of chlorination adopted will depend, of course, on the products required. But the usual conditions employed are those yielding the maximum of monochlorobenzene. Various forms of chlorination plant are described in Cain's " Manufacture of Intermediate Products for Dyes," pp. 7-10. The essential features of the preparation are as follows :

The benzene to be chlorinated, which must be pure and dry, is stirred rapidly with about 1 per cent. of its weight of wrought-iron powder in a vessel fitted with a reflux

condenser, and is heated to boiling. Dry chlorine is passed slowly through. The hydrochloric acid formed is led off through vessels containing water, in which it is absorbed. Chlorine is passed until the increase in weight corresponds to that required for monochlorobenzene, or, say, about 35 parts for every 78 parts of benzene used. The product is then fractionated, about 80 per cent. being obtained as monochloro-benzene, 10 to 15 per cent. as *p*-dichlorobenzene, 1 to 3 per cent. as *o*-dichlorobenzene, and about 5 per cent. as recovered benzene.

B. The Nitrochlorobenzenes.

Monochlorobenzene, on nitration in the usual way with mixed nitric and sulphuric acids, yields nitrochlorobenzenes. Using one molecular equivalent of nitric acid, a nearly theoretical yield of a mixture of *o*- and *p*-nitrochlorobenzenes is obtained, only a minute proportion of the meta compound being formed.

o-**Nitrochlorobenzene,** needle-shaped crystals, m.p. 32·5°, b.p. 245·5° (753 mm.), 119° (8 mm.).

p-**Nitrochlorobenzene,** prisms or leaflets, m.p. 83°, b.p. 238·5 (753 mm.), 113° (8 mm.); $D_{18°}$ 1·52.

The following table, given by Holleman (*Proc. K. Akad. Wetensch.*, Amsterdam, 1904, **7**, 266), shows the solidifying points of mixtures of the two substances, and serves as a guide in their separation :

Per Cent. of Para.	Solidifying Point (Degrees).	Per Cent. of Para.	Solidifying Point (Degrees).
0	32·09	35·43	18·43
1·05	31·06	37·53	21·90
4·60	29·92	39·96	26·10
6·54	29·00	41·67	28·50
8·88	27·89	45·86	33·98
12·61	26·10	48·94	37·65
16·26	24·19	60·18	50·10
19·22	22·65	64·66	54·32
22·91	20·75	68·54	57·83
26·89	18·30	70·02	59·22
30·26	16·29	71·93	60·80
32·39	15·35	75·48	63·97
32·71	14·94	81·93	69·10
32·90	14·85	86·70	72·77
33·07	14·77	90·30	75·40
33·10	14·65	95·57	79·13
34·09	16·73	100·00	82·15
34·94	17·47		

From the table it is seen that the eutectic point is 14·65°, corresponding to a composition of 33·1 per cent. of para, and 66·9 per cent. of ortho compound. In Holleman's experiments the product of nitration had a solidifying point of about 59°, which corresponds to a mixture of 70 per cent. para and 30 per cent. ortho compound. From such a mixture on cooling to about 16°—*i.e.*, a little above the eutectic point— most of the para compound crystallises out and can be separated from the still liquid
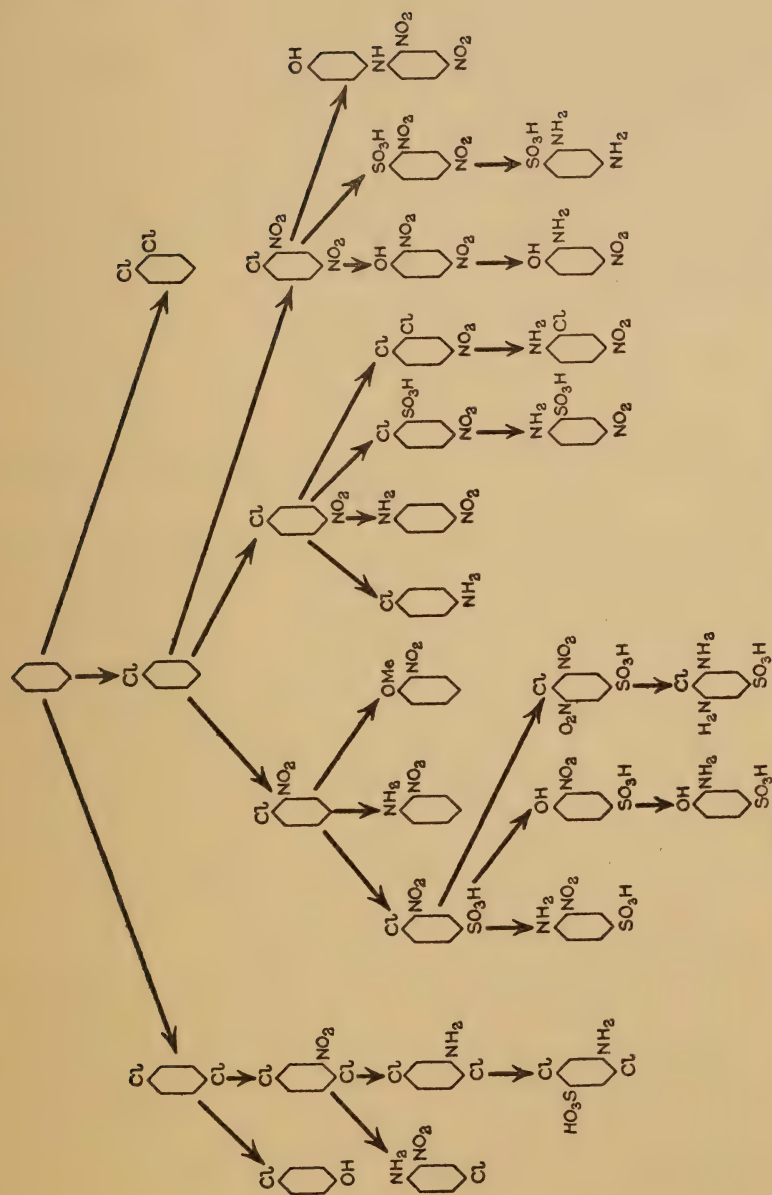
CHART I.—CHLOROBENZENES AND THEIR DERIVATIVES.

portion by centrifuging. The liquid mixture, according to a patent of the Griesheim Elektron (G.P. 97013), can be further separated into its components by systematic fractional distillation and crystallisation. The boiling-point difference under 8 mm. pressure is only 6°, but the first fraction is richer in para and the last is richer in ortho compound than the eutectic mixture, so that on cooling these, pure para compound crystallises out from the former and pure ortho compound from the latter. By a repetition of these processes a fairly complete separation is obtained.

Either of the two nitrochlorobenzenes, on further nitration, yields 2 : 4-dinitro-chlorobenzene, but this compound is usually prepared by the direct nitration of chlorobenzene.
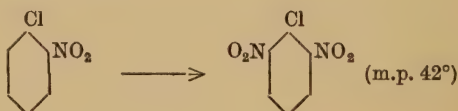
2 : 4-**Dinitrochlorobenzene**—
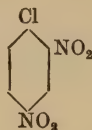
—forms large rhombic crystals, m.p. 51°, b.p. 315° (with slight decomposition), D^{22} 1·697. Soluble in alcohol. It has an extremely irritant action on the skin and should be handled with care.

The following method of preparation is given by Fierz-David (" Farbenchemie," 1920, p. 108): 350 gms. of mixed acid containing 50 per cent. HNO_3 is stirred in an iron nitrating vessel and cooled to 5°. 113 gms. of chlorobenzene is dropped in slowly, with rapid stirring, the temperature being maintained below 5°. After all the chloro-benzene has been added, the mixture is stirred for one hour, during which the temperature may be allowed to rise to 10°. It is then slowly raised to 50° and maintained for one hour at this temperature. Up to this point, nitration has only proceeded as far as the mononitro stage. 350 gms. of concentrated sulphuric acid is then dropped in very cautiously with vigorous stirring, and the mixture is finally heated for half an hour at 115° to complete the dinitration. After cooling, the product is poured into 2 litres of water, in which the dinitrochlorobenzene solidifies to a pale yellow cake. This is separated, melted under water to remove acid, and is thus obtained practically pure. The yield is 200 gms., or nearly theoretical.

In large scale practice, where both mono and dinitrochlorobenzenes are made, the crude mixture of o-nitrochlorobenzene with some p-compound (obtained as above described after separation of as much as possible p-nitrochlorobenzene) is nitrated under approximately the same conditions as apply to the nitration of nitrobenzene to dinitrobenzene. This arrangement uses up the o-nitrochlorobenzene, which finds relatively little application as compared with p-nitrochlorobenzene. The o-compound nitrates more readily than the p-, but naturally shows some tendency to nitrate in the second o-position as well as in the p- —

—whereas *p*-nitrochlorobenzene should give only the one product, the second nitro group entering either of the two *o*-positions.

2 : 4-Dinitrochlorobenzene has proved an exceedingly useful intermediate on account of the reactivity of its chlorine atom, which is caused by the presence of the two nitro groups in the *o*- and *p*-positions. The chlorine is easily displaced, for instance, by —OH, through the action of dilute alkali, even sodium carbonate being sufficient, thus yielding 2 : 4-dinitrophenol, the intermediate for Sulphur Black T. Again, the action of ammonia and primary amines produces dinitroaniline and a number of very useful diphenylamine derivatives :

$$(NO_2)_2.C_6H_3.Cl \quad + \quad NH_2R \quad \longrightarrow \quad (NO_2)_2C_6H_3.NH.R$$
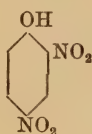
The preparation of these derivatives will be dealt with later. They are generally used for the production of sulphur colours.

By condensing 2 : 4-dinitrochlorobenzene with *p*-aminodiphenylamine derivatives, yellow dyes of the nitro class are obtained.

C. Derivatives of 2 : 4-Dinitrochlorobenzene.
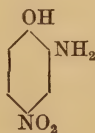
2 : 4-**Dinitrophenol**—

—pale yellow crystals, m.p. 114°, easily crystallised from water, since it dissolves in 21 parts of boiling water, but requires 197 parts of water at 18°. Its solubility in alcohol is about equal to that in water. It is easily soluble in ether, chloroform, and benzene.

It is prepared by boiling 100 parts of 2 : 4-dinitrochlorobenzene with a solution of 125 parts of sodium carbonate (as Na_2CO_3, or an equivalent of soda crystals) in 1,000 parts of water, until the oily drops of dinitrochlorobenzene completely disappear. This may take a considerable time, but can be hastened by very rapid stirring. The solution now contains the sodium salt of dinitrophenol, and on cooling and acidifying the dinitrophenol separates almost pure. The yield is nearly theoretical.

2 : 4-Dinitrophenol is used only as an intermediate for sulphur colours. By heating it with sodium sulphide and sulphur under various conditions of concentration, temperature and duration of heating, black dyes of different shades and properties are formed.
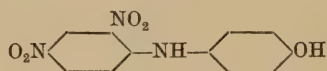
p-**Nitro**-*o*-**aminophenol**—

—yellow-brown leaflets from water. The crystals which contain water of crystallisation melt at 80° to 90°. The anhydrous substance melts at 142° to 143°.

This substance has been prepared by Anwers and Röhrig (*Ber.*, **30**, 995) by reduction of 2 : 4-dinitrophenol with ammonium sulphide in very dilute aqueous alcoholic solution, the nitroaminophenol being extracted with ether. The yield obtained was only 32 per cent.

An improved method of preparation is given in G.P. 289454, in which the reduction is performed by means of iron filings and sulphur dioxide. A mixture of 184 gms. of dinitrophenol, 1,000 c.c. of water, and 200 gms. of iron filings, is stirred and heated to 80° to 90°, and at this temperature sulphur dioxide is passed in until the iron is almost entirely dissolved. The brown liquid obtained is freed from the remaining iron by filtration, and air is then blown through until no more substance separates. The nitroaminophenol is thus obtained as a brown crystalline powder. The yield is 60 per cent.

p-Nitro-*o*-aminophenol, like other *o*-aminophenol derivatives, is used as a first component in monoazo dyes, these having the property of dyeing chrome-mordanted wool, or of being developed by afterchroming.

2 : 4′-**Dinitro-4′-hydroxydiphenylamine**—

—forms red leaflets, m.p. 190°, soluble in alkalies.

This substance is prepared by condensing dinitrochlorobenzene with *p*-aminophenol as follows: 202 gms. of dinitrochlorobenzene, 150 gms. of *p*-aminophenol (about 30 per cent. excess), and 1,500 c.c. of alcohol are heated in a flask fitted with reflux condenser on the water-bath till complete solution is obtained. 150 gms. of crystalline sodium acetate is added, when a deep orange-red colour is produced. Under the influence of the sodium acetate condensation proceeds quickly, and after an hour's further heating, is complete. On cooling, most of the product crystallises out, and is filtered off and washed with alcohol. From the filtrate a further quantity is obtained by distilling off about half the alcohol and cooling. This second crop contains some sodium chloride, which is washed out with water.

This intermediate is probably the most important of those diphenylamine derivatives obtained from dinitrochlorobenzene, which, as previously mentioned, serve for the production of sulphur colours by heating with sodium sulphide and sulphur in different solvents, such as alcohol carbon disulphide, etc.
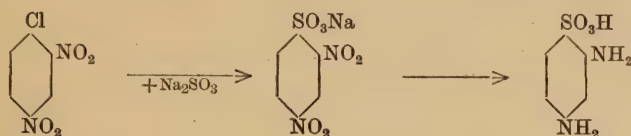
m-**Phenylenediamine-4-sulphonic acid:**
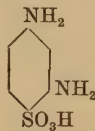
The acid crystallises from water in tabular crystals, which soon turn brown in the air.

This acid is derived from 2 : 4-dinitrochlorobenzene by a method due to Erdmann, G.P. 65240 :

The following process, based on Erdmann's method, somewhat modified, is described by Fierz-David ("Farbenchemie," 1920, p. 59): 202 gms. of dinitrochlorobenzene are mixed with 500 gms. of methylated spirit (not denatured with pyridine bases). To this is added the equivalent of 80 gms. of SO_2 in the form of a concentrated solution of sodium sulphite. This solution is most conveniently prepared from the commercial 35 per cent. bisulphite solution by adding an equivalent of 40 per cent. caustic soda, the end point being such that phenolphthaleïn is faintly reddened. The mixture is now heated to boiling on the water-bath with stirring for five hours. On cooling, the dinitrosulphonate separates as yellow crystals.

Instead of distilling off the alcohol as directed in the patent, the crystals are filtered off, pressed, and then redissolved in water and reduced by the method used in the case of m-dinitrobenzene (p. 20). The solution of m-phenylenediaminesulphonic acid so obtained is evaporated to 400 c.c. and 100 gms. of salt added. Hydrochloric acid is then added until Congo paper is just turned faint violet (not blue). After standing for two days, the separated sulphonic acid is filtered off, washed with a very little water, and dried. The yield is 125 gms. of the pure acid, or 66 per cent. of the theoretical.

It is important to note that traces of copper or iron in the reaction mixture may prevent any of the dinitrosulphonic acid from being formed.

D. Derivatives of p-Nitrochlorobenzene.

p-**Chloroaniline—**

—rhombic prisms, m.p. 69·7°. The sublimed substance melts at 70° to 71°. B.p. 232·3°. Forms a sulphate, $(Cl.C_6H_4.NH_2)_2.H_2SO_4$, which is sparingly soluble in cold water.

This substance is obtained by reducing p-nitrochlorobenzene with iron filings and hydrochloric acid as in the preparation of aniline from nitrobenzene. Bashioum and Powers (*J. Ind. Eng. Chem.*, 1923, **15**, 408) suggest, as the best proportions in this case, 15 parts of 35 per cent. hydrochloric acid, 15 parts of water, and 100 parts of nitro compound, the mixture being refluxed while 100 parts of iron filings are gradually added. The distillate in the condenser appears red until reduction is complete, when it becomes colourless. It was found to be necessary to remove any unnitrated

chlorobenzene from the nitrochlorobenzene, or reduction was retarded to a remarkable degree. After completion of the reduction, the acid is neutralised, and the *p*-chloroaniline separated by steam distillation.

*p*-**Nitroaniline**—

$$\text{NH}_2 - \bigcirc - \text{NO}_2$$

—yellow crystals, m.p. 147°, soluble in 45 parts of water at 100°, and in 1,250 parts at 12°. Easily soluble in alcohol. It is not volatile in steam.

It is possible to replace the chlorine of *p*-nitrochlorobenzene almost quantitatively by NH_2, by heating with aqueous ammonia in an autoclave at moderately high temperatures, a process which was patented by the Clayton Aniline Co. in 1902 (E.P. 24869[02]; G.P. 148749). While such displacements of chlorine by ammonia and primary amines are generally facilitated by the presence of small amounts of copper compounds, as discovered by Ullmann, a copper catalyst is not necessary in this case, and, in fact, contact with copper is actually deleterious to the product. The same applies to iron and lead. This necessitates the use of enamelled autoclaves, which are expensive and difficult to keep in good repair. In spite of these difficulties, however, the process seems to have become established on the manufacturing scale, though it has not entirely displaced the older process in which acetanilide is nitrated (p. 36).

Pure *p*-nitrochlorobenzene is heated with excess of a concentrated aqueous solution of ammonia in an enamelled autoclave at 170° for hours. The ammonia used must be free from pyridine bases, otherwise brown impurities are formed, which are difficult to remove. The conversion is generally practically complete, but any unchanged chloro-body may be removed by steam distillation, and after cooling, the *p*-nitroaniline is filtered off and dried. A very pure product is obtained by this method.

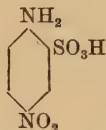*p*-**Nitrochlorobenzenesulphonic acid** :

$$\text{Cl} - \bigcirc \begin{matrix} \text{SO}_3\text{H} \\ \text{NO}_2 \end{matrix}$$
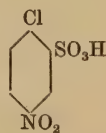
The acid forms large triclinic plates with $2H_2O$, sparingly soluble in water and alcohol. The sodium salt crystallises with $1H_2O$, as needles or leaflets, and is fairly soluble in water. The chloride of the acid melts at 89° to 90°, and the amide at 185° to 186°.

Ullmann and Jüngel (*Ber.*, 1909, **42,** 1077) give the following method of preparation : 157·9 parts of *p*-nitrochlorobenzene is stirred with 200 volume-parts of 20 per cent. oleum at 160° for six hours. After cooling, the mixture is run into 425 parts of ice. A brown solution is at first formed, from which the acid crystallises out on standing. It is filtered off, washed with dilute hydrochloric acid, redissolved in

boiling water, steam passed through to drive out a little unchanged nitrochlorobenzene, and on cooling the pure acid crystallises out, the crystallisation being assisted by adding concentrated hydrochloric acid.   The yield is 246 parts, or 91 per cent.

Fierz-David uses a larger proportion of acid (100 gms. of monohydrate with 280 gms. of 25 per cent. oleum to 100 gms. of nitrochlorobenzene) and sulphonates at a lower temperature, 100° to 110°.   After pouring the sulphonation mixture on to 300 gms. of ice and 300 gms. of water, the product is salted out with 200 gms. of salt.

p-**Nitroaniline**-*o*-**sulphonic acid** :

$$NH_2$$
$$SO_3H$$
$$NO_2$$

This compound is prepared by heating *p*-nitrochlorobenzene-*o*-sulphonic acid with ammonia in an autoclave.   If alcoholic ammonia is used, two to three hours at 120° to 140° is sufficient (Fischer, *Ber.*, 1891, **24**, 3789).   But the use of alcohol is unnecessary.   The moist press-cake of sulphonic acid obtained in the sulphonation of *p*-nitrochlorobenzene is stirred into its own weight of 20 per cent. aqueous ammonia and heated in an autoclave at 150° for eight hours.   The pressure developed is six atmospheres.   On cooling, the ammonium salt of the nitroanilinesulphonic acid crystallises out in large amber-coloured cubes.   From 100 gms. of *p*-nitrochlorobenzene, a yield of 100 gms. of the ammonium salt is obtained (Fierz-David, " Farbenchemie," 1920, p. 61).

This intermediate is used as a first component in monoazo dyes, one of which, with β-naphthol as second component, is a red lake pigment.   It may also be used for polyazo dyes by reducing the nitro group in the first formed monoazo dye and then diazotising the aminoazo compound and coupling with a third component, as in Carbon Black.

1 : 2-**Dichloro**-4-**Nitrobenzene**—

$$Cl$$
$$Cl$$
$$NO_2$$

—long needles, as crystallised from alcohol, m.p. 43°, b.p. 256° to 260°.

The chlorination of *p*-nitrochlorobenzene to produce this substance is described in G.P. 167297.   20 parts of *p*-nitrochlorobenzene are heated to 95° to 120°, 1 part of anhydrous ferric chloride added, and 4·37 parts of chlorine passed into the molten substance.   The liquid is then poured into cold water, and the dichloronitrobenzene washed with water at 50°.   It is purified by crystallisation from alcohol.

As catalysts, instead of the ferric chloride, antimony pentachloride (3 parts), iodine (2 parts), or phosphorus pentachloride (5 parts), may be used, though in the last case chlorination must be carried out at 150°.

By heating 1 : 2-dichloro-4-nitrobenzene with alcoholic ammonia at 190° for

forty-eight hours, *o*-chloro-*p*-nitroaniline is obtained (*Rec. trav. chim.*, **36**, 135, 155) :

$$\text{Cl, Cl, NO}_2 \longrightarrow \text{NH}_2, \text{Cl, NO}_2$$

o-Chloro-*p*-nitroaniline crystallises in yellow needles, m.p. 107°.

It is used as a component in trisazo dyes of the type of Diamine Green B. Diazotised *o*-chloro-*p*-nitroaniline is coupled in acid solution with H-acid, and the product coupled with diazotised benzidine on one side in alkaline solution, the other side being then coupled with phenol or salicylic acid.

E. Derivatives of *o*-Nitrochlorobenzene.

o-**Nitrochlorobenzene** is readily sulphonated in the usual way by heating with five times its weight of 30 per cent. oleum on the water-bath. It is, therefore, more easily sulphonated than its isomer *p*-nitrochlorobenzene, which requires a much higher temperature. The sulphonic acid is isolated as usual by liming out and converting to the sodium salt (Fischer, *Ber.*, 1891, **24**, 3186). The derivative so formed is *o*-Nitrochlorobenzene-*p*-sulphonic acid :
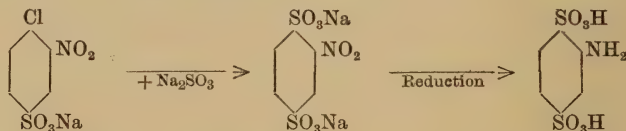
$$\text{Cl, NO}_2, \text{SO}_3\text{H}$$
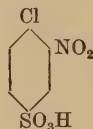
The free acid crystallises in needles with $1\text{H}_2\text{O}$. The barium salt forms yellow leaflets with $1\text{H}_2\text{O}$, almost insoluble in alcohol. The chloride melts at 40° to 41°. The amide, yellow prisms from alcohol, melts at 175° to 176°.

The labile nature of the chlorine atom in the above compound is made use of in several ways, of which mention may be made first of the preparation of aniline-2 : 5-disulphonic acid—

$$\text{NH}_2, \text{SO}_3\text{H}, \text{HO}_3\text{S}$$
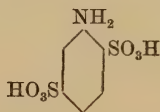
—as indicated in the following scheme :

$$\text{Cl, NO}_2, \text{SO}_3\text{Na} \xrightarrow{+ \text{Na}_2\text{SO}_3} \text{SO}_3\text{Na, NO}_2, \text{SO}_3\text{Na} \xrightarrow{\text{Reduction}} \text{SO}_3\text{H, NH}_2, \text{SO}_3\text{H}$$

Details are given in G.P. 77192 (Badische).

(*a*) **Nitrobenzene**-2 : 5-**disulphonic acid.**—20 kg. of sodium *o*-nitrochlorobenzene-*p*-sulphonate is dissolved in 50 litres of water, 30 kg. of crystalline sodium sulphite

added, and the solution boiled for one to two hours under reflux. On cooling, part of the disulphonate crystallises out and most of the remainder is separated by addition of salt. After filtering, the product is pressed and dried. It is not necessary to purify it for the next stage, but it may be purified by crystallisation from dilute alcohol. It forms needles, soluble in cold water, but insoluble in absolute alcohol. On boiling the aqueous solution with caustic soda, an orange precipitate is formed.

(*b*) **Reduction.**—32 kg. of the crude nitro compound is dissolved in 200 litres of water, 10 litres of 30 per cent. acetic acid added, the solution stirred on the boiling water-bath, and reduced with 30 kg. of iron powder. When the reduction is finished the solution is made alkaline with soda, filtered, evaporated to some extent, and acidified. On cooling the product crystallises out as the acid sodium salt, forming colourless short needles.

The chlorine atom may also be replaced by hydroxyl, by heating the chloronitro-benzenesulphonic acid with caustic alkali (G.P. Anm. B. 15933), thus yielding *o*-nitro-phenol-*p*-sulphonic acid:

$$
\begin{array}{c}
\text{OH} \\
\text{NO}_2 \\
\text{SO}_3\text{H}
\end{array}
$$
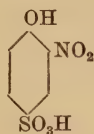
This is said to be the technical method of preparing this substance, but no details of the process have been published. Presumably the method is similar to that by which 2 : 4-dinitrophenol is formed from 2 : 4-dinitrochlorobenzene (p. 5).

On reduction, *o*-nitrophenol-*p*-sulphonic acid gives *o*-aminophenol-*p*-sulphonic acid:

$$
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{SO}_3\text{H}
\end{array}
$$
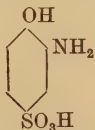
The reduction is stated by Post (*Ann.*, **205**, 51) to be best carried out with tin and hydrochloric acid.

Another method of preparation of *o*-aminophenol-*p*-sulphonic acid is given on p. 94.

o-Nitrochlorobenzene-*p*-sulphonic acid may also be nitrated further to produce 1-chloro-2 : 6-dinitrobenzene-4-sulphonic acid:

$$
\begin{array}{c}
\text{Cl} \\
\text{O}_2\text{N} \quad \text{NO}_2 \\
\text{SO}_3\text{H}
\end{array}
$$
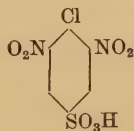
The introduction of a second nitro group into a nitrochlorobenzene is not an easy matter. A relatively high temperature must be used, and the composition of the nitrating acid so arranged that no free water is present before the nitration is finished.

The method is given in G.P. 116759 : 27·5 parts of the potassium salt of o-nitrochloro-benzene-p-sulphonic acid are dissolved in 100 parts of 25 per cent. oleum, then 15 parts of 87 per cent. nitric acid are gradually added. The solution is then heated to 120° to 130° for some time. When the nitration is finished, the solution is poured into water, and the crystallised product which separates is filtered off.

The substance may also be prepared directly from chlorobenzene in one operation according to the scheme :
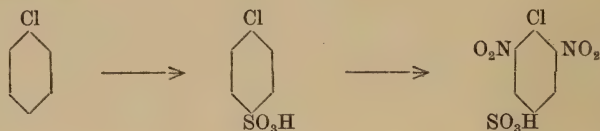
34 parts of chlorobenzene are mixed with 72 parts of monohydrate and 30 parts of 25 per cent. oleum, and the mixture is stirred on the water-bath until the chlorobenzene has disappeared owing to sulphonation. The solution is now cooled and 26 parts of 87 per cent. nitric acid added slowly, so that the temperature does not rise above 40°, after which the solution is allowed to stand for two hours. In order to introduce the second nitro group, 100 parts of 60 per cent. oleum and 40 parts of potassium nitrate are added, and the mixture heated at 120° to 130° for two to three hours. The product is then isolated as before.

The above substance can be reduced to the corresponding diamino compound (G.P. 150373) 1-chloro-2 : 6-diaminobenzene-4-sulphonic acid :
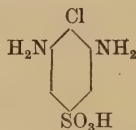
10 parts of the potassium salt of the dinitro compound are treated with 80 parts of concentrated hydrochloric acid (D 1·19). The mixture is well stirred and 20 parts of granulated tin gradually added. Much heat is developed, and a yellow solution is formed. On cooling, a tin chloride double salt of the diamino compound separates in colourless needles. These are filtered off, dissolved in a large volume of hot water, and hydrogen-sulphide passed until the tin is completely precipitated. The tin sulphide is filtered off, and on cooling the filtrate deposits the diamino compound as colourless needles.

1-Chloro-2 : 6-diaminobenzene-4-sulphonic acid is almost insoluble in cold water, and rather sparingly in hot water. The acid crystallises with $1H_2O$. The sodium and potassium salts are readily soluble. The substance diazotises readily to give a tetrazo compound.

o-Nitrochlorobenzene may also be amidated to o-nitroaniline :
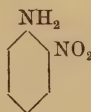
160 gms. of *o*-nitrochlorobenzene and 300 gms. of aqueous ammonia (D 0·880) are heated in an autoclave for four hours at 170° to 175°.   The pressure at first rises to 48 atmospheres, but later, as amidation proceeds, falls to 30 atmospheres.   After cooling, the *o*-nitraniline is filtered off, washed with a little water, and purified by recrystallising from 7 litres of boiling water.   The yield is about 90 to 95 gms. *o*-Nitraniline forms orange-red needles, m.p. 72°, moderately soluble in boiling water, but sparingly in cold water.   It is somewhat volatile in steam.

By another replacement of the chlorine atom in *o*-nitrochlorobenzene, there is obtained *o*-nitroanisole :

$$\begin{array}{c} OCH_3 \\ NO_2 \end{array}$$
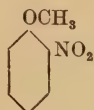
This is accomplished by heating with sodium or potassium methylate.   The preparation, using methyl alcohol and aqueous caustic potash under ordinary pressure, is described by Brand (*J. pr. Chem.*, 1903 (ii), **67**, 145).   While this method works well with   some   nitrochloro   compounds—*e.g.*, with   2 : 4-dinitrochlorobenzene—it is apparently better to use water-free sodium methylate in this case.   The preparation is described by Fierz-David ('' Farbenchemie,'' second edition, 1923, p. 81) as follows :

Into a litre autoclave in an oil-bath put 600 c.c. of dry methyl alcohol in which previously 23 gms. of sodium has been dissolved.   Add 158 gms. of pure *o*-nitrochlorobenzene and heat in the well-closed autoclave, raising the temperature during the first hour to 120°, keeping at this temperature for three hours, and finally for a further hour at 128°.   The pressure developed is 8 to 10 atmospheres.   Blow the methyl alcohol off through a good condenser (the recovered alcohol can be used again without treatment).   The residual crude product is washed twice with five times its volume of hot water, separated from the water, and distilled *in vacuo*.   It boils at 141° under 15 mm.   The yield is 136 gms. or 88 per cent.

Another method of preparation of *o*-nitroanisole is given on p. 85.

F. Derivatives of *p*-Dichlorobenzene.

p-**Chlorophenol**—

$$\begin{array}{c} OH \\ Cl \end{array}$$

white crystals, m.p. 37°, b.p. 217°, $D^{20·5}$ 1·306.   It is almost insoluble in water, but easily soluble in alcohol and ether.   It is insoluble in carbonate solutions.

G.P. 281175 describes the preparation as follows : 30 parts of *p*-dichlorobenzene, 36 parts of solid caustic soda, and 70 parts of ordinary methyl alcohol (not specially dried) are heated together in an iron autoclave at 190° to 195° for forty hours.   The *p*-chlorophenol produced is purified by distillation.   The yield is about 90 per cent.

The function of the methyl alcohol is presumably that of solvent, but the use of other solvents—*e.g.*, benzene—gives lower yields.   Using aqueous caustic soda, no chlorophenol is produced.

p-Chlorophenol is used in the preparation of quinizarin (p. 208).

Nitration of *p*-dichlorobenzene yields one mononitro derivative : 1 : 4-dichloro-2-nitrobenzene :
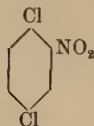
The dichlorobenzene is nitrated with 1·5 parts of a mixture containing 2 parts of nitric acid (D 1·54) to 3 parts of concentrated sulphuric acid.   After mixing at the ordinary temperature the reaction is finished on the water-bath (Morgan and Norman, *J.C.S.*, 1902, **81**, 1382).   The product is isolated in the usual way.   It forms white crystals, m.p. 54·5°, b.p. 266°, D^{22} 1·669.   It is sparingly soluble in cold alcohol, easily in hot alcohol and in benzene.

It can be reduced by iron and hydrochloric acid, following the method used for the reduction of nitrobenzene to aniline, and thus yields 2 : 5-dichloroaniline—
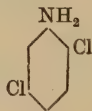
—which forms white crystals, m.p. 50°, b.p.$_{744}$ 246°.

On sulphonating this dichloroaniline, the sulpho group enters the *p*-position to the amino group, yielding 2 : 5-dichloroaniline-4-sulphonic acid :
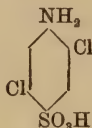
The sulphonation was carried out by Noteling and Kopp (*Ber.*, 1905, **38**, 3513) by adding 40 gms. of 2 : 5-dichloroaniline to 120 gms. of 18 per cent. oleum and heating the solution at 170° to 180° for about two hours.   When sulphonation was complete, on pouring the solution on ice, the sulphonic acid separated.   By using 20 to 25 per cent. oleum, the sulphonation may be carried out at 120° (G.P. 222405).

This dichloroanilinesulphonic acid yields a hydrazine derivative which, condensed with acetoacetic ester, forms a pyrazolone derivative.

1 : 4-Dichloro-2-nitrobenzene may also be converted by the action of ammonia into *p*-chloro-*o*-nitroaniline :
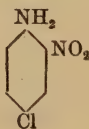
This forms orange-red needles, m.p. 116·5°, and resembles *o*-nitraniline strongly in properties including smell, solubility in water and volatility in steam.

Dichloronitrobenzene is dissolved in sufficient alcohol and heated with excess of aqueous ammonia in an autoclave at 190° for eight hours.   The yield is quantitative (Green and Rowe, *J.C.S.*, **103,** 897).

This chloronitroaniline is used in making a yellow lake pigment, Lithol Fast Yellow GG, by condensing two molecular proportions of it with one of formaldehyde. The resulting compound has the constitution :

$$\text{Cl}\langle\ \rangle\text{NH---CH}_2\text{---NH}\langle\ \rangle\text{Cl}$$
$$\qquad\quad \text{NO}_2 \qquad\qquad\qquad \text{NO}_2$$
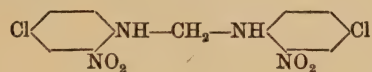
CHAPTER II

NITROBENZENE AND ITS DERIVATIVES

NITROBENZENE is one of the fundamental intermediates for dyestuffs (and for other products), and its manufacture is therefore a matter of considerable importance, but a detailed description of it would be beyond the scope of this book. Such a description will be found in " Aniline and its Derivatives," by P. H. Groggins, and in the *Chemical Trade Journal*, 1906, **38,** 59. The essentials only of the ordinary process will be given here.

Nitrobenzene—

—a colourless highly refractive liquid with a characteristic smell; m.p. 3·6°, b.p.$_{760}$ 209°, b.p.$_{18}$ 96°; D_{15}^{15} 1·2093. It is very slightly soluble in water, and also dissolves water to a very slight extent, but mixes in all proportions with alcohol, ether, and benzene.

The benzene used for its preparation should be free from the usual impurities. It should boil within 0·2° (which excludes homologues), should solidify to a white crystalline mass on cooling in ice, be free from carbon disulphide and thiophene, and contain no unnitratable hydrocarbons. The nitration is carried out with a mixture of nitric and sulphuric acids of the following composition :

HNO_3	..	..	..	..	..	..	30 per cent.
H_2SO_4	..	..	..	..	..	..	58 ,,
H_2O	..	..	..	..	..	..	12 ,,

The mixed acid is made up from nitric and sulphuric acids of any convenient strengths available. Usually 75 per cent. nitric acid and 95 per cent. sulphuric acid are used, these being mixed in the ratio of 11 parts of the nitric to 17 parts of the sulphuric acid. 280 parts of the above mixed acid are used for every 100 parts of benzene.

The benzene is placed in an iron vessel fitted with a rapid stirrer, a thermometer, and arrangements for heating and cooling. Rapid efficient stirring is necessary, since benzene does not dissolve in the mixed acid, and the two liquids must be thoroughly emulsified in order to obtain smooth nitration with no side reactions. The mixed acid is added to the benzene at such a rate that the temperature chosen for the nitration is reached, but not exceeded. The temperature of nitration may be varied within fairly wide limits without harm to the product, but the tendency at present is to conduct the nitration at the maximum permissible temperature, and therefore at the highest possible speed in order to obtain maximum production per unit of plant. At 30° the nitration takes seven to eight hours, at 50° about two to three hours. An upper limit of 80° is fixed by the boiling-point of benzene, but this is not approached in practice because of the danger of forming dinitrobenzenes.

16

CHART II.—NITROBENZENE AND ITS DERIVATIVES.

(See Chart III.)

2

When the mixed acid has all been run in, stirring is continued till the nitration has reached the desired point. On the large scale this can be determined by drawing off a sample from time to time, allowing it to settle, separating the upper layer of nitrobenzene, and determining the percentage of nitric acid remaining in the lower acid layer by means of a Lunge nitrometer. When the residual nitric acid falls to 1 per cent., the operation is ended. Using the quantities of benzene and mixed acid given above, the result is that a small proportion of benzene remains unattacked. This is desirable in order to avoid formation of dinitrobenzene.

After allowing the mixture to settle, the upper layer of nitrobenzene has a specific gravity of about 1·235, which is higher than that of pure nitrobenzene, owing to some dissolved acid. The lower acid layer consists of approximately 74 per cent. sulphuric acid, which is sufficiently dilute to attack iron, though not very rapidly, and the nitrating vessel on the large scale is, therefore, sometimes lead-lined. The acid, after denitration and concentration, is used again.

The nitrobenzene after separation from the acid is washed with water, then with dilute caustic soda solution, and finally again with water. The small proportion of benzene remaining in it is separated by steam distillation, the passage of steam being continued till the oily drops of distillate, the first of which float in water, begin to sink quickly. This distillate is separated and used in a succeeding nitration.

The crude nitrobenzene obtained in this way is pure enough, provided a pure benzene was used in its preparation, for ordinary purposes, such as nitration to dinitrobenzene, reduction to aniline, etc. But for the " Oil of Mirbane " of perfumery it is distilled *in vacuo*. If thiophene was present in the benzene used, this is nitrated to dinitrothiophene, and the presence of this substance in the nitrobenzene is shown by shaking an alcoholic solution of it with alcoholic potash, when a red colouration is produced.

Further nitration of nitrobenzene yields principally *m*-dinitrobenzene, though some *o*- and *p*-dinitrobenzenes are also formed at the same time. The reaction has been studied by Holleman (*Ber.*, 1906, **39**, 1715), who found that a nearly constant proportion, about 91 to 93 per cent. of the meta compound was formed under varying conditions, while the proportions of the ortho and para compounds varied considerably, though their total amount remained nearly constant.

m-**Dinitrobenzene**—
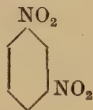
—colourless or faintly yellow crystals (plates), m.p. 89·7°, b.p. $_{770·5}$ 302·8°, b.p. $_{33}$ 188°. It is soluble in benzene and toluene. 100 parts of benzene at 18·2° dissolve 39·45 parts of *m*-dinitrobenzene. (*o*-Dinitrobenzene melts at 116·5°, *p*-dinitrobenzene at 171° to 172°.)

It is not usual to prepare dinitrobenzene directly from benzene in one operation, but instead to nitrate further the crude mononitrobenzene. This second nitration

requires more drastic conditions than the first—viz., a higher temperature (115°), and a more concentrated mixed acid. The mixed acid used has the composition:

H_2SO_4 ..	..	..	..	..	..	..	71 per cent.
HNO_3 ..	..	..	..	..	..	..	22 ,,
H_2O ..	..	..	..	..	..	..	7 ,,

To the crude nitrobenzene obtained from 100 parts of benzene previously heated to 100°, 450 parts of mixed acid of the above composition is added with good stirring, the rate of addition being regulated so as to allow the temperature to rise slowly to 115°, and to remain at this point during the remainder of the nitration. When the acid has all been added, stirring is continued until the nitration is finished, which is indicated by a sample solidifying when cooled. The stirrer is now stopped and the reaction mixture allowed to settle. The molten dinitrobenzene forms the upper layer, the lower acid layer having a specific gravity of about 1·8 and consisting of a mixed acid containing 87 per cent. H_2SO_4 and 3 to 4 per cent. HNO_3. After cooling to about 70°, the acid layer is run off and the dinitrobenzene run into well-stirred boiling water in order to extract the acid from the product. The washing is repeated, with addition of alkali to the water, till the product is completely acid-free. It is then separated and dried. As obtained in this way, the dinitrobenzene melts at 75° to 80° and contains some o- and p-dinitrobenzenes. It should not smell of nitrobenzene. It is purified by recrystallisation from the least possible quantity of benzene or toluene.

As *m*-dinitrobenzene is extremely poisonous, great care must be taken in handling it.

Reduction of *m*-dinitrobenzene with an alkaline sulphide, such as sodium or ammonium sulphide, leads to *m*-nitroaniline—
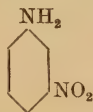
—yellow needles, m.p. 114°; 100 parts of water at 24° dissolve 0·12 part of *m*-nitroaniline, but its solubility in boiling water is much greater.

Technically, the reduction is carried out by means of sodium sulphide or disulphide. If sodium sulphide is used, 1·5 molecules are required for the reduction of one nitro group, but the nature of the oxidation products of the sulphide apparently has not been accurately determined. Some sulphur generally separates during the reaction and probably thiosulphate is also formed. On the other hand, if the reduction is performed with sodium disulphide, the reaction is simpler, and only 1 molecule of the disulphide is required for the reduction of one nitro group:

$$R.NO_2 + Na_2S_2 + H_2O \longrightarrow R.NH_2 + Na_2S_2O_3$$
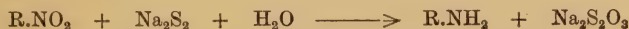
An account has been given by Cobenzl (*Chem. Zeit.*, 1913, **37**, 299) of the preparation of *m*-nitroaniline using the disulphide, which seems successful on a large scale.

10 kg. of *m*-dinitrobenzene is stirred vigorously in 400 litres of boiling water in an iron vessel till it is thoroughly emulsified. A solution is made up of 15 kg. of crystalline sodium sulphide ($Na_2S.9H_2O$) and 4 kg. flowers of sulphur in 65 litres of water. Only 2 kg. of sulphur are required to form the disulphide with the above quantity of sodium sulphide, but the extra sulphur, while apparently not taking part in the reaction, is found in practice to be necessary for complete reduction. The disulphide solution is run into the dinitrobenzene-water mixture at such a rate as not to stop the boiling. A further boiling of fifteen to twenty minutes completes the reduction, the *m*-nitraniline formed all going into solution, while the excess sulphur separates. The liquid is then filtered hot (the residual sulphur can be used again), and on cooling the filtrate *m*-nitraniline crystallises out fairly pure. The crystals are centrifuged and washed alkali-free with cold water. The yield of crystallised *m*-nitraniline is about 6·6 kg. or 80 to 82 per cent. of the theoretical, provided a good quality of dinitrobenzene is used.

Cobenzl's remarks on the subject of yield in relation to quality of starting material are instructive and may be taken as illustrative of a general rule. For example, crude dinitrobenzene is sometimes yellow in colour and evil-smelling, due to the presence of trinitrobenzene and phenols. Such a starting material was found to give a 50 per cent. yield of *m*-nitraniline containing tarry impurities. The same starting material could be purified considerably, at the expense of a 10 per cent. loss in weight, by treatment with hot soda solution, which decomposed the trinitrobenzenes and dissolved out the phenols, yielding a white odourless product. This purified material now gave a yield of 76 to 78 per cent. of *m*-nitraniline.

m-Nitraniline is used as a first component in azo dyes mostly of the monoazo class.

When the reduction of *m*-dinitrobenzene is carried out in an acid medium—*e.g.*, in the ordinary way using iron and hydrochloric acid—both nitro groups are reduced, yielding *m*-phenylenediamine—
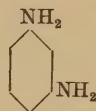
—rhombic crystals, m.p. 63°, b.p. 287°, D^{15} 1·1389. The base is very soluble in water, alcohol, and ether. It forms a dihydrochloride, which crystallises in fine needles, and is very soluble in water. It may be diazotised in solution in concentrated hydrochloric acid, and then yields a tetrazo compound; but if diazotisation is attempted in the ordinary dilute solution, brown azo dyes (Bismarck Brown) are formed, due to coupling of the partially diazotised base with the remainder. The base quickly turns brown in the air.

The process of reduction does not differ essentially from the usual acid iron reduction, which is described in detail under Aniline (p. 26). It need only be mentioned that the quantities required per gram-molecule (168 gms.) of dinitrobenzene are :

1½ litres of water;
300 gms. of fine iron;
20 c.c. of concentrated HCl.

Care must be taken when reduction is finished to precipitate any dissolved iron completely by boiling with sufficient soda. After filtering hot, the solution is made just acid with hydrochloric acid.

The base is not usually isolated from solution, but if desired it may be obtained by evaporating the solution *in vacuo* till it contains about 40 per cent. of the base, and on cooling in ice this deposits the base in the form of prismatic crystals containing $\frac{1}{2}H_2O$. Any isomers present remain in the mother liquor.

The critical point in the preparation of *m*-phenylenediamine (and of other diamines and aminophenols) comes at the moment when the solution is made alkaline in order to rid it of iron. Oxidation is apt to be serious at this point, resulting in brown or even black products, especially if the starting material were not pure. A process has been patented in G.P. 269542 which avoids this difficulty, though only at the expense of using a hundred times the quantity of acid required in the ordinary process. The separation of the reduction product depends on the fact that the hydrochlorides of diamines are almost insoluble in concentrated hydrochloric acid. As applied to *m*-phenylenediamine, the process is as follows :

100 gms. of *m*-dinitrobenzene are added to 1,270 c.c. of 30 per cent. hydrochloric acid and the mixture warmed to 40° to 50°. 247 gms. of iron in as pure a form as possible (small iron nails weighing three to a gram are recommended) are added gradually with good stirring. The heat of reaction raises the mixture to boiling-point. The iron almost all dissolves, and on cooling, *m*-phenylenediamine dihydrochloride separates in white crystals, which are filtered off and dried.

m-Phenylenediamine is used as an end component in azo dyes of many different types. It couples very readily in weak acid solution with diazo compounds, a noteworthy feature of the resulting dyes being that almost all are brown in shade, even when there are two or three other components of the most varied nature. It is possible to couple two molecules of diazo compound in succession with one molecule of *m*-phenylenediamine, the resulting disazo compound having one of two formulæ :
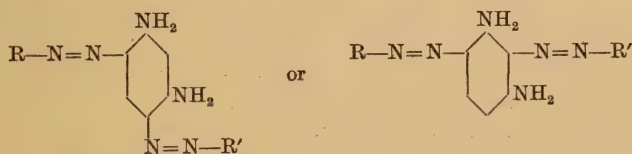
Azo dyes containing *m*-phenylenediamine as end component may, therefore, be developed on the fibre, without much change of shade, by coupling a convenient diazo compound with them. These complex dyes are also produced in substance.
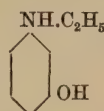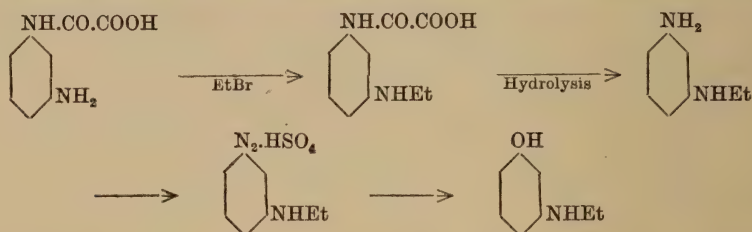
m-**Phenylenediamineoxamic acid**—
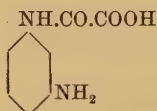
—crystallises in fine needles from water in which it is sparingly soluble even at the boil. M.p. 225° (decomp.). The sodium and ammonium salts are soluble in water.

The mono-oxamic acids of diamines in general are formed by heating the diamines with *aqueous* oxalic acid. According to Klusemann (*Ber.*, 1874, **7**, 1261), *m*-phenylene-diamineoxamic acid is prepared by gradually adding a solution of *m*-phenylenediamine to a boiling solution of oxalic acid. The oxamic acid separates as a grey precipitate from the boiling solution. The oxalate of *m*-phenylenediamine, formed as an intermediate stage, is much more soluble than the oxamic acid.

Ethyl-*m*-aminophenol—

$$\overset{\text{NH.C}_2\text{H}_5}{\underset{\text{OH}}{\bigcirc}}$$

This substance, which is more usually prepared by other methods, has been made from the above oxamic acid (G.P. 76419, Badische) by the following series of reactions :

$$\overset{\text{NH.CO.COOH}}{\underset{\text{NH}_2}{\bigcirc}} \xrightarrow{\text{EtBr}} \overset{\text{NH.CO.COOH}}{\underset{\text{NHEt}}{\bigcirc}} \xrightarrow{\text{Hydrolysis}} \overset{\text{NH}_2}{\underset{\text{NHEt}}{\bigcirc}}$$

$$\longrightarrow \overset{\text{N}_2.\text{HSO}_4}{\underset{\text{NHEt}}{\bigcirc}} \longrightarrow \overset{\text{OH}}{\underset{\text{NHEt}}{\bigcirc}}$$

The sodium salt of *m*-phenylenediamineoxamic acid (20 kg.) is ethylated by heating with 11 to 12 kg. of ethyl bromide and 20 kg. of alcohol in an autoclave at 120° to 150° for six to eight hours. The alcohol is then distilled off and the residue extracted with cold water to remove sodium bromide, the ethylated *m*-phenylene-diamineoxamic acid remaining undissolved. This is boiled with 3 to 4 parts of water and 1 part of sulphuric acid for a considerable time, and the water then mostly boiled off. The residual solution of ethyl-*m*-phenylenediamine sulphate is cooled with ice and diazotised with one molecular proportion of sodium nitrite. The solution of diazo compound is then warmed until evolution of nitrogen ceases. After neutralising with carbonate, the ethylaminophenol may be extracted with ether or benzene and isolated in the usual way.

Another method of preparation of ethyl-*m*-aminophenol is given on p. 56.

Sulphonation of Nitrobenzene.

The sulphonation of nitrobenzene yields chiefly *m*-nitrobenzenesulphonic acid, which forms about 90 per cent. of the sulphonation product. Not more than 10 per cent. of the ortho and para isomers are produced. It is of interest, however, to note here that if benzenesulphonic acid is nitrated the proportions of the three isomers are considerably different.

***m*-Nitrobenzenesulphonic acid :**

$$\overset{\text{NO}_2}{\underset{\text{SO}_3\text{H}}{\bigcirc}}$$
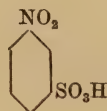
123 parts of nitrobenzene are dropped slowly into about 350 parts of 25 per cent. oleum previously heated to 70° and well stirred. The rate of addition is so controlled that the temperature rises to about 100°, and is maintained at 100° to 110° till all the nitrobenzene has been added. Thereafter the temperature is kept at 110° to 115°, till a test portion of the liquid dissolves almost entirely in water and does not smell of nitrobenzene. More oleum is added, if required, to complete the sulphonation. The solution is now cooled and poured on to 500 parts of ice, well stirred. The sulphonic acids dissolve up completely to a hot solution, but a little sulphone—

$$\text{NO}_2 \qquad \text{NO}_2$$
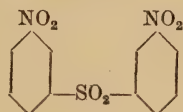
—which is always formed, remains undissolved, and this is filtered off. To the well-stirred hot filtrate, salt is slowly added till the sodium salt of m-nitrobenzenesulphonic acid is as completely salted out as possible. About 200 parts of salt are required. After stirring for several hours while cooling the mass is filtered and pressed so as to expel acid liquors as much as possible. The press-cake contains, besides sodium m-nitrobenzenesulphonate, a little of the isomeric sulphonates and some sodium sulphate.

The nitrosulphonate is not usually dried or purified, but is reduced directly to metanilic acid—

$$\text{NH}_2$$
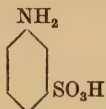
—long needles, soluble in water. 1 part dissolves in 68 parts of water at 15°.

The press-cake of nitrobenzenesulphonate obtained, as just described, is dissolved up in the minimum quantity of boiling water, the solution stirred rapidly, and cast-iron filings added gradually, while boiling is maintained till the reduction is complete. This is ascertained by spotting the liquid on filter-paper, when a colourless rim should be shown. About 130 parts of iron are required. The acid adhering to the press-cake is sufficient for the reduction. The liquid is now neutralised with soda, and boiling is continued until any dissolved iron compounds are decomposed and the iron all precipitated as hydroxide. The liquid is filtered hot, the filtrate evaporated to 600 volatile parts, and hydrochloric acid added till the solution is acid to Congo paper. On cooling, the metanilic acid crystallises out.

Owing to the comparative solubility of metanilic acid, a substantial amount remains in solution, and for this reason the acid is not usually isolated, the solution being used directly for the preparation of dyestuffs. The yield is estimated by diazotisation of a known volume of the solution with standard nitrite solution. It amounts to about 90 per cent. of the theoretical. The result obtained by titration with nitrite is, however, somewhat too high, since any sulphanilic and o-aminobenzene-sulphonic acids present are also diazotised. It should be noted, too, that the presence

of these isomers may sometimes appreciably affect the shades of the dyestuffs prepared from the metanilic acid.

Metanilic acid is used as first component in azo dyes of the mono- and disazo classes.

Sodium metanilate, when fused with caustic soda at high temperatures, yields *m*-aminophenol—

$$NH_2 \quad OH$$
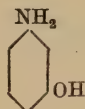
—white crystals, m.p. 122° to 123°, easily soluble in ether and alcohol, moderately soluble in hot water (it readily forms supersaturated solutions), sparingly soluble in benzene, and insoluble in ligroin. If pure it is stable in air.

The N-acetyl derivative, $C_6H_4(OH)NHAc$, melts at 148° to 149°. The hydrochloride forms prisms, m.p. 229°.

The method of preparation is described in G.P. 44792, as follows: 20 parts of caustic soda are melted up with 4 parts of water, and the temperature raised to 270°. 10 parts of well-dried sodium metanilate are gradually added, and the temperature of the melt is then maintained at 280° to 290° for one hour. The cold melt is dissolved in water, the solution acidified with hydrochloric acid, and any resinous matter filtered off. The filtrate is neutralised with sodium bicarbonate, which sets free the aminophenol. This is then extracted with ether and isolated in the usual way.

Another method of preparation of *m*-aminophenol, starting from resorcinol, is described on p. 101.

m-Aminophenol is used mostly as a hair and fur dye, but has also been used as second component in a monoazo dye.

4-Nitroaniline-3-**sulphonic acid :**

$$NH_2 \quad SO_3H \quad NO_2$$
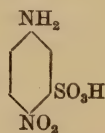
The acid crystallises in pale yellow needles, sparingly soluble in cold water, moderately in hot water.

This substance is prepared by nitrating the acetyl derivative of metanilic acid (Eger, *Ber.*, 1888, **21**, 2579).

Sodium metanilate is boiled with two molecular proportions of acetic anhydride, and the resulting thick paste of the acetyl derivative is dissolved in five times its weight of sulphuric acid. To the well-cooled solution, the calculated quantity of nitric acid (D 1·385), dissolved in four times its weight of sulphuric acid, is slowly added. The mixture is allowed to stand two to three hours. It is then poured on ice, and the yellow nitrometanilic acid (hydrolysis has taken place), which separates on standing, is filtered off. It is recrystallised from water and dried at 120°.

It is used in preparing nitro-*m*-phenylenediamine :

$$NH_2$$
$$NH_2$$
$$NO_2$$
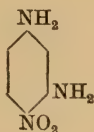
The preparation is carried out, according to G.P. 130438 (A.G.F.A.) by amidation of 4-nitroaniline-3-sulphonic acid with ammonia. This is an unusual reaction in the benzene series, though common in the anthraquinone series.

4-Nitroaniline-3-sulphonic acid is heated with four times its weight of 25 per cent. ammonia in an autoclave at 170° to 180° for three hours. On cooling, most of the nitrophenylenediamine crystallises out as yellowish-red prisms, m.p. 161°. It is soluble also in alcohol and ether.

Nitro-*m*-phenylenediamine is used as an end component in azo dyes in conjunction with benzidine and other diamines as first components, the resulting dyes being bright yellow or orange in shade.

Reduction of Nitrobenzene.

Nitrobenzene (and aromatic nitro compounds generally) can be reduced by stages, according to the conditions employed, to a series of different products, whose relations are shown approximately in the following scheme :

$$R.NO_2 \longrightarrow R.NO \longrightarrow R.NHOH$$
$$R.N{-}N.R$$
$$O$$
$$R.N{=}N.R \rightleftharpoons R.NH.NH.R$$
$$R.NH_2$$
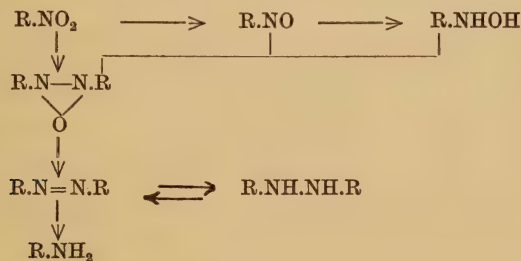
Whether the reduction will proceed wholly to the amino compound (in this case aniline), or will stop at one of the intermediate stages, depends on at least two factors—(1) the condition of the reaction medium as regards alkalinity or acidity, (2) the temperature. The azoxy and azo stages are favoured by an alkaline medium, the hydroxylamine stage by neutral conditions, and reduction to the amino compound by acid conditions, though the acidity need only be slight, that given by solutions of the salts of the heavier metals, such as iron and zinc, being sufficient. Of the various reduction products, the amino compounds are most important from the dyestuffs' point of view, while the azo and hydrazo compounds are also of importance in the present and a few other cases, because they are intermediary to the formation of benzidine and its derivatives.

The reduction of nitrobenzene to aniline will be dealt with first.
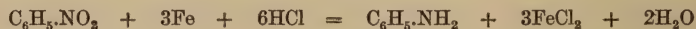Aniline—

$$NH_2$$

—a colourless oil turning brown in sunlight.   Freezes at $-6.24°$ C., b.p. $184.32°$ to $184.39°$ at 760 mm., D_{15}^{5} 1.0268, n_D^{20} 1.5850.

The reduction of nitrobenzene to aniline is commonly carried out by means of iron and hydrochloric acid or ferrous chloride.   Details with regard to plant used, etc., are given in " Aniline and its Derivatives," by P. H. Groggins, and in the *Chemical Trade Journal*, 1906, **38**, 59.

The quantity of acid required is much less than that indicated by the equation :

$$C_6H_5.NO_2 \; + \; 3Fe \; + \; 6HCl \; = \; C_6H_5.NH_2 \; + \; 3FeCl_2 \; + \; 2H_2O$$

In practice only about 3 per cent. of the hydrochloric acid indicated by the equation is used, and the end product, apart from the aniline, is chiefly magnetic iron oxide, Fe_3O_4.   Several theories have been proposed to explain the mechanism of this reaction. The facts appear to be that before the reduction commences ferrous chloride is formed by reaction between the iron and the acid, that at the beginning of the reduction some ferric hydroxide can be observed, and that at the end almost all the iron is in the form of the oxide Fe_3O_4.   The formation of the ferric hydroxide possibly takes place thus—

$$C_6H_5.NO_2 \; + \; 2Fe \; + \; 4H_2O \; = \; C_6H_5.NH_2 \; + \; 2Fe(OH)_3$$
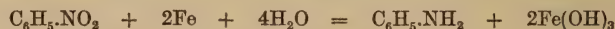
—this reaction being accelerated by the ferrous chloride present.   How the ferric hydroxide is converted to the oxide Fe_3O_4 is not known.   However, the reaction, as a whole, may be considered as following the equation :

$$4C_6H_5.NO_2 \; + \; 9Fe \; + \; 4H_2O \; \xrightarrow[\text{Catalysed by FeCl}_2]{} \; 4C_6H_5.NH_2 \; + \; 3Fe_3O_4$$
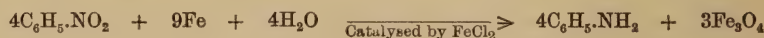
The reduction is carried out in a cast-iron vessel fitted with a stirrer and a reflux condenser, arrangements being made for the gradual addition of nitrobenzene and iron borings.   These borings must be of cast-iron (steel being useless for this purpose), and they are previously ground in a disintegrator.

For the reduction of 100 parts of nitrobenzene the reducing vessel is first charged with about 110 parts of iron borings (this being about a tenth of the total amount of iron to be used), 120 parts of 30 per cent. hydrochloric acid, and 60 parts of water. The mixture is stirred and heated to the boil (usually by passing in steam through the stirrer, which is made hollow for the purpose).   This preliminary operation is spoken of as " etching " the iron by the acid—that is, the iron is supposed to be brought into a more active condition suitable for initiating the reduction.   A more rational view is that in this operation there is formed the ferrous chloride required for catalysis of the reaction between the nitrobenzene, iron and water.

The nitrobenzene is now run in, accompanied by the main quantity of iron borings

in small quantities, at such a rate that the reaction proceeds steadily, as observed by the rate of refluxing of the mixture of nitrobenzene, aniline, and water. As the reaction is strongly exothermic, external heating is unnecessary, on the large scale at any rate, and, in fact, the addition of nitrobenzene and iron may require slowing off at times owing to the violence of the reaction. Too violent a reaction leads to over-reduction of the nitrobenzene with production of benzene. After all the iron and nitrobenzene have been added, external heating is recommenced in degree sufficient to keep the mixture refluxing until the reduction is completed. This is recognised by the condensate, which is at first orange, then yellow, becoming water-white in colour.

The contents of the reducing vessel now are aniline, water containing some ferrous chloride in solution, and iron oxide, this last being in the form of a fine black powder. The separation of the aniline is most simply and easily done by steam distillation, the weight of steam required being about six times the weight of the aniline. The distillate separates into a lower layer of aniline, containing about 5 per cent. of water in solution (together with any benzene formed in the reduction or contained in the original nitrobenzene), and an upper layer consisting of a 3 per cent. solution of aniline in water. The upper layer is run off, and the aniline layer is distilled under reduced pressure. The first fraction contains water, benzene, and some aniline, and this is returned to the steam distillation receivers for separation of the aniline. The remainder of the distillate is pure aniline.

In the regular working of the above process, the aqueous layer of the steam distillate is used, partly to supply the water for charging the reducing vessel at the beginning of the reduction, and partly, by boiling in a separate boiler, to supply the steam required for the succeeding steam distillation. The quantity of aniline contained in this water is, therefore, kept in circulation in the process, and on a normal run with this arrangement the whole of the aniline produced by the reduction of the charge of nitrobenzene can be isolated. The yield of aniline from 100 parts of nitrobenzene is 71·5 to 72 parts or about 95 per cent. of the theoretical.

Modifications of the Ordinary Process.

Economic considerations have led to various suggested modifications of the above process with regard to the separation of the aniline from the reaction mixture. These modifications have in view the reduction or elimination of the cost of dealing with the relatively large quantities of water required by the steam distillation.

(*a*) The contents of the reducing vessel may be distilled directly under reduced pressure.

(*b*) The iron oxide may be filtered off, the aniline and water separated, and the aniline distilled.

(*c*) Ordinary steam from the boiler plant may be used entirely for the steam distillation, and most of the aniline recovered from the aqueous layer by a double extraction with the nitrobenzene, which is afterwards to be reduced (G.P. 282531). The water containing any residual aniline is run to waste.

Which, if any, of the above modifications is worth adoption is a matter of comparative costs, and need not be further dealt with here. These points are fully considered in " Aniline and its Derivatives," by P. H. Groggins, pp. 35-57.

Alternative Processes.

(*a*) A large number of patents have been taken out for the reduction of nitrobenzene in the form of vapour by metallic catalysts. Nickel, copper, iron, cobalt, platinum, silver, and gold have all been proposed, generally at temperatures of over 200°.*

G.P. 282492 (Meister Lucius and Brüning) is exceptional in claiming to accomplish the reduction at 120° with finely divided nickel. Steam and hydrogen are passed through nitrobenzene, and the mixed vapours led through a tube containing the nickel contact mass at 120°, the passage of the vapours being regulated so that no nitrobenzene escapes reduction. The yield is said to be quantitative. If these claims can be sustained, the process seems to be a very convenient one, with the great advantage over the usual process of being continuous.

(*b*) The amidation of chlorobenzene by ammonia has been attempted, but without success. Apparently Ullmann's discovery of the activating effect of copper and its salts on the replacement of halogen by the amino group suggested the application of the method to this case. G.P. 204951 claims an 80 per cent. yield of aniline from chlorobenzene by heating with ammonia and copper sulphate in an autoclave at 180° to 200° for twenty hours. This claim has been examined by Quick (*J. Am. Chem. Soc.*, 1920, **42,** 1033), who was only able to obtain a maximum yield of 39 per cent. of aniline.

The applications of aniline to the preparation of other intermediates are dealt with in Chap. III. Its direct applications as a dyestuff intermediate are numerous and varied.

(i.) It is used as a first component in mono-, dis-, and trisazo dyes, but never as an end component, owing to difficulty in coupling and to its tendency to form diazoamino compounds which do not readily transform.

(ii.) Triphenylmethane dyes of the Pararosaniline or Magenta type are made from aniline by an empirical method in which aniline and *p*-toluidine (to supply the " methane carbon ") are heated with an oxidising agent. Aniline is further used to phenylate the amino groups in Pararosaniline, and thus form the Aniline Blues.

(iii.) Many dyes of the azine class, such as Safranine, are obtained by oxidising mixtures of aniline with various *para*-diamines. An empirical condensation of aniline with aminoazobenzene yields the Indulines, dyestuffs also of the azine class. Oxidation of aniline with nitrobenzene or nitrophenol produces the Nigrosines, and oxidation of aniline hydrochloride on the fibre forms Aniline Black.

* See G.P. 139457 (F.P. 312615); E.P. 13149 and 15334 of 1914; E.P. 5692 and 6409 of 1915 (G.P. 282568; U.S.P. 1207802); E.P. 16936 and 22523 of 1913 (F.P. 458033; U.S.P. 1247629); G.P. 282492; F.P. 462006; G.P. 281100; G.P. 263396; *cf. also* Brown and Henke, *Journ. Phys. Chem.*, 1922, **26, 161.**

(iv.) Aniline is also used in making acid wool dyes of the anthraquinone series, by condensing it with chloro- or hydroxy-anthraquinones. By elimination of HCl or H_2O, phenylaminoanthraquinones are formed, and on sulphonating these (the sulpho group entering the phenyl nucleus), the acid dyes are produced.

The various products of alkaline reduction of nitrobenzene owe their technical interest to the fact that they are stages in the preparation of hydrazobenzene, which, by the action of aqueous acid solutions, is transformed by intramolecular change into benzidine—

$$C_6H_5.NH.NH.C_6H_5 \longrightarrow H_2N.C_6H_4—C_6H_4.HN_2$$
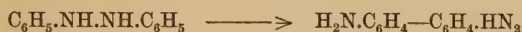
Benzidine—

—crystallises in leaflets from water, m.p. 127·5 to 128°, b.p. $_{740}$ 400° to 401°. Its solubility in water at 12° is 1 part in 2,447, but in boiling water 1 part in 106·5. It is easily soluble in alcohol.

Sulphate, $C_{12}H_{12}N_2.H_2SO_4$, forms small glittering scales, almost insoluble in boiling water and in alcohol.

Hydrochloride, $C_{12}H_{12}N_2.2HCl$, forms leaflets, easily soluble in water, but precipitated from solution by concentrated hydrochloric acid. On boiling a solution of the dihydrochloride, the monohydrochloride is formed as sparingly soluble needles.

The **monoacetyl** derivative melts at 198°, the **diacetyl** at 317°.

It will be most convenient to deal with the preparation of benzidine in two stages, of which the first is concerned with the formation of hydrazobenzene, and the second with its transformation to benzidine.

(a) **Hydrazobenzene.** The older process, as described by Schultz ("Chemie des Steinkohlenteers," 1900, I., p. 93), carries out the reduction to the hydrazo compound in one operation by means of zinc dust and alcoholic caustic soda. A mixture of 100 kg. of nitrobenzene and 50 kg. of alcohol is heated under a reflux condenser and to the boiling liquid 150 to 160 kg. of zinc dust are added, followed by slow addition over three or four hours of a mixture of 100 kg. of alcohol and 13 kg. of caustic soda solution (36° Bé). Boiling is continued until a test portion is found to be light grey in colour. If this point is not reached within half an hour after all the caustic soda has been added, 20 kg. of water are added and boiling continued, more zinc dust being added, if necessary, to complete the reduction. The alcohol is then distilled off with steam. The residual mixture contains crystalline hydrazobenzene, zinc hydroxide, sodium zincate, and unchanged zinc. It is transferred to a fine sieve, on which the hydrazobenzene is retained, the remaining solids passing through. It is well washed with water. The hydrazobenzene may also be freed from zinc, etc., by diluting the mixture and cooling to 10° to 15° by ice, followed by careful addition of just sufficient cold hydrochloric acid to dissolve out the zinc. The moist hydrazobenzene is used directly for the transformation to benzidine.

This process works well, and may be made to give an almost quantitative yield of

hydrazobenzene, but it has been displaced by processes in which the comparatively expensive alcohol and zinc dust are dispensed with. Nitrobenzene may be reduced to hydrazobenzene by cast-iron borings and aqueous caustic soda, as described in G.P. 138496 (Weiler-ter-Meer). The quantity of iron required bears no calculable relation to that suggested by any theory of the reaction, since the reduction is a surface effect. For this reason the iron must be ground as fine as possible. Oil and grease must be removed, and the iron is also previously etched by heating with concentrated caustic soda.

According to the patent just mentioned, reduction with iron and caustic soda has also the advantage of proceeding by definite stages—

Nitrobenzene ———> azoxybenzene ———> azobenzene ———> hydrazobenzene

—at any one of which the reaction may be stopped, by use of the appropriate quantity of iron and caustic soda, and the product extracted by stirring with a hydrocarbon solvent, such as benzene, from which it is easily recovered. The reduction by stages is effected as follows : 100 kg. of nitrobenzene and 750 kg. of iron borings are stirred together and warmed to about 90°, when 800 kg. of 60 per cent. caustic soda is added gradually and the temperature maintained at 100° to 120°. Very powerful stirring apparatus is, of course, required with such a thick, heavy mixture. The course of the reaction may be observed by the change of colour and by disappearance of the smell of nitrobenzene, but a more exact indication may be obtained in large scale working by observation of the setting-points of samples withdrawn at intervals. Thus, nitrobenzene has a setting-point of 5°. As the reduction proceeds, this falls to a minimum of – 13°, corresponding to a 40 per cent. conversion to the azoxy compound. The setting-piont then rises to a maximum of 31°, at which point, if the smell of nitrobenzene has disappeared, formation of azoxybenzene is complete. Reduction may now be continued as far as the azo compound by adding 250 kg. of iron and 300 kg. of 60 per cent. caustic soda and stirring further at the same temperature as before. The setting-point sinks again to 25°, then rises to 63°, when reduction to azobenzene is finished. Addition of another 250 kg. of iron and 300 kg. of caustic soda solution, with continued heating and stirring, carry the reduction on to the hydrazobenzene as indicated by the setting-point which, after falling to 55°, finally rises to 122° to 125°. Towards the end the temperature must either be raised to 130°, or a solvent added in order to prevent the mass from solidifying. This last stage is the most difficult to carry through satisfactorily, partly owing to the tendency for the reduction to proceed too far and form aniline (this can be minimised by lowering the temperature to 80° and adding benzene as solvent for the hydrazobenzene), and partly to the tendency towards formation of inseparable emulsions. The quantities of iron given are, of course, only rough approximations, the actual quantities required depending on the fineness of division.

Fierz-David ("Farbenchemie," 1920, p. 72) prefers, as a laboratory method, to carry the reduction by means of iron and caustic soda only as far as azobenzene, which is then isolated by extraction with benzene and evaporation of the benzene solution. Reduction to hydrazobenzene is then carried out in alcohol with zinc dust

and 30 per cent. caustic soda at 60° or under. On filtering (and boiling out the zinc residues with some fresh 90 per cent. alcohol), the filtrate separates into two layers of which the lower contains aqueous sodium zincate, while the upper is an alcoholic solution of hydrazobenzene. This layer is separated, saturated with carbon dioxide to precipitate alkali, and the filtered solution evaporated to obtain the hydrazobenzene, of which a quantitative yield is obtained.

In E.P. 203059 (Murdoch and Galbraith), the use of sodium amalgam is proposed for the reduction of nitro compounds to hydrazo compounds. A suitable amalgam is that obtained from the cathode chamber of a Castner-Kellner cell in which brine is electrolysed. The nitro compound, mixed with water containing a water-miscible solvent for the nitro body, such as pyridine, is brought into effective contact with the amalgam, either by allowing the solution to flow in a thin film over the amalgam or by dropping the amalgam through the well-stirred solution, the spent amalgam being drawn off continuously through a **U**-tube at the bottom of the vessel.

(b) The transformation of hydrazobenzene to benzidine has been studied by Holleman and van Loon (*Proc. K. Akad. Wet.*, Amsterdam, 1903, **6,** 262), and by van Loon (*Rec. trav. chim.*, 1904, **23,** 62), who find that the amount of benzidine obtained is independent of the nature of the acid used, that it diminishes as the temperature is raised, and that it increases at first with increasing concentration of acid, but decreases above a certain acid concentration.

A small proportion of the *o-p*-diamino compound, diphenyline—
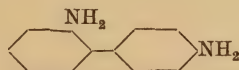
—is always formed, together with traces of aniline. The optimum conditions of transformation yield about 85 per cent. of benzidine and 10 to 15 per cent. of diphenyline. In practice hydrochloric acid is used for the transformation, and this should be free from sulphuric acid since benzidine sulphate is insoluble, and it is advantageous to dissolve the benzidine completely when formed in order to free it from insoluble impurities carried by the hydrazobenzene.

The moist hydrazobenzene obtained by any of the methods previously described is added gradually to a quantity of 30 per cent. hydrochloric acid (1·2 molecules), sufficient to ensure a definitely acid solution at the end of the reaction. During the addition the temperature is kept down by addition of ice. After stirring for several hours in the cold to complete the change, the mass is heated to 80° to bring all the benzidine and diphenyline into solution, any insoluble matter is filtered off, and the benzidine precipitated as sulphate by adding sulphuric acid or sodium sulphate or bisulphate. The sulphate of diphenyline is soluble. The benzidine sulphate is filtered off and washed thoroughly with water containing a little sulphuric acid. Without drying, the sulphate is then stirred up with water and soda solution added till alkaline, the benzidine base being then filtered off, washed and dried. It is finally purified by vacuum distillation.

Benzidine is used as a first component in the preparation of azo dyestuffs. Its

tetrazo compound couples readily with amines and phenols, yielding azo compounds which are substantive colours for cotton, a property which constitutes the great value of benzidine as an intermediate. This property of yielding direct cotton colours apparently depends, in part at least, on the fact that the amino groups are both in the para position to the diphenyl linkage, since diphenyline does not possess the property.

Several substitution products of benzidine are made with a view to modifying the shade or solubility of the azo colours derived from them. But it is found that in some cases the affinity of the dyes for cotton is also considerably affected. Generally substitution in the ortho positions to the amino groups leaves the affinity for cotton of the derived dyes unchanged or even increases it somewhat. This applies to benzidine-3 : 3′-disulphonic acid, 3 : 3′-dichlorobenzidine, 3 : 3′-dinitrobenzidine, o-tolidine, and dianisidine (the last two, however, are not prepared from benzidine, but from the corresponding nitrobenzene derivatives, and will be dealt with later). On the other hand, in benzidine-2 : 2′-disulphonic acid, the affinity of the derived dyes for cotton is much diminished, and in 2 : 2′-dinitrobenzidine, it has entirely disappeared. The dyes derived from these *meta*-substituted benzidines, however, dye wool. The substantive property is restored if the *meta*- substituents form a new ring, as in benzidine sulphone and in diaminocarbazole :

Benzidine sulphone   Diaminocarbazole
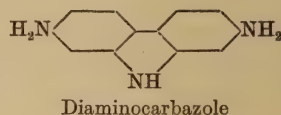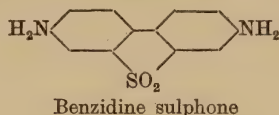
Benzidinesulphonic Acids.

These are prepared by the action of concentrated sulphuric acid and oleum on benzidine at high temperatures, but it is rather difficult to obtain individual products.

Benzidine-3-sulphonic acid :

The acid is very sparingly soluble even in boiling water, and almost insoluble in alcohol and ether. It forms a hydrochloride.

This acid is best prepared by the bake process, as described in G.P. 44779 (*Ber.*, **22**, 2461). Benzidine sulphate is stirred with $1\frac{1}{2}$ molecular proportions of H_2SO_4 as dilute acid and the mixture evaporated to dryness. The powdered substance is spread on enamelled trays and heated in an air-oven at 170° for twenty-four hours. The black mass so obtained is ground up, extracted with dilute alkali, and filtered. The filtrate is made just acid with acetic acid which precipitates the monosulphonic acid, but leaves any disulphonic acid in solution as sodium salt.

Benzidine-3 : 3′-disulphonic acid :

The acid forms small white leaflets without water of crystallisation. It is almost insoluble in water.

One part of benzidine sulphate is heated with 2 parts of concentrated sulphuric acid at 210° for thirty-six to forty-eight hours. The product is diluted with water, the solution made alkaline and filtered. Any monosulphonic acid present is first precipitated by addition of acetic acid and is filtered off. On making the filtrate mineral-acid, the disulphonic acid is precipitated. The yield is given as 90 per cent. (*Ber.*, **14**, 300; **22**, 2463; G.P. 44779).

Benzidine sulphone—

$$H_2N \underset{SO_2}{\diagdown} NH_2$$
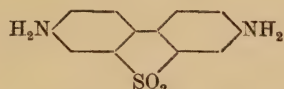
—forms fine bright yellow leaflets, almost insoluble even in boiling water and alcohol. Its salts are dissociated by water.

Formation of the sulphone is favoured by use of oleum. The preparation is described in G.P. 33088 (*Ber.*, **22, 2467**). Benzidine sulphate is added to excess of 20 per cent. oleum and the mixture is warmed on the water-bath until benzidine can no longer be detected in a test portion. The cooled solution is then poured on ice, allowed to stand twelve hours, and the benzidine sulphone sulphate $(C_{12}H_{10}N_2.SO_2.H_2SO_4 + 1\frac{1}{2}H_2O$, is filtered off. Some unchanged benzidine sulphate is always present. The salt is decomposed by hot dilute caustic soda solution, and the precipitated sulphone is extracted with alcohol. It is then further purified by conversion to the hydrochloride.

Benzidine sulphone disulphonic acid :

$$\underset{H_2N}{\overset{HO_3S}{\diagdown}} \underset{SO_2}{\overset{SO_3H}{\diagup}} NH_2$$
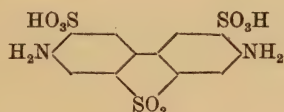
The acid crystallises in pale yellow prisms with $\frac{1}{2}H_2O$. It is moderately soluble in hot water if this is acid-free, but the addition of mineral acid renders it practically insoluble. Its sodium salt crystallises in yellow needles, which are sparingly soluble in cold water, but easily soluble in hot.

It may be prepared directly from benzidine without isolation of the sulphone (*Ber.*, **22,** 2469; G.P. 27954). One part of benzidine is heated with 4 parts of 40 per cent. oleum for some time at 100° in order to form the sulphone. The solution is then raised to 150°, and kept at this temperature until a test portion on dilution and addition of alkali no longer precipitates sulphone. The solution is then poured on ice, when the disulphonic acid is precipitated along with some monosulphonic acid and a little unchanged sulphone, while any tri- and tetrasulphonic acids remain dissolved. The precipitate is filtered off, then dissolved in dilute caustic soda solution, filtered, and the monosulphonic acid precipitated by making acid with acetic acid. This is filtered off and the disulphonic acid is now separated by addition of hydrochloric or sulphuric acid. The yield is 80 per cent.

The azo dyes from this intermediate are substantive to cotton and also dye wool. The dyeings on wool are specially fast to milling.

3 : 3′-**Dichlorobenzidine**—

$$H_2N \overset{Cl}{\diagup}\!\!\!\diagdown \!\!\!-\!\!\!\overset{Cl}{\diagup}\!\!\!\diagdown NH_2$$

—crystallises in needles, m.p. 133°, almost insoluble in water, but soluble in alcohol, benzene, and glacial acetic acid. Its hydrochloride, $C_{12}H_{10}N_2Cl_2.HCl$, crystallises from alcohol in needles, and is precipitated from its aqueous solutions by strong hydrochloric acid. The sulphate, nitrate, and oxalate are very sparingly soluble, even in boiling water.

The preparation from benzidine is described in G.P. 94410 (Levinstein). Benzidine is first converted into the diacetyl derivative by boiling with glacial acetic acid in the usual way. 26·8 kg. of diacetylbenzidine are dissolved in two to three times its weight of 90 per cent. sulphuric acid and the solution poured into ice water, the object being to obtain as fine a suspension of the substance as possible. The suspension is cooled to 0°, stirred and sufficient 10 per cent. bleach or hypochlorite solution to give 4 molecular proportions of active chlorine is slowly run in. An intense green colouration appears at first, but this vanishes later and towards the end the dichlorodiacetyl compound has completely separated as a crystalline yellow precipitate. The mass is then warmed to 40° and filtered. The product is hydrolysed by boiling with four times its weight of 20 per cent. hydrochloric acid under reflux for three hours, or, at any rate, until a test portion dissolves completely in dilute hydrochloric acid. The solution is then diluted with water, and either the hydrochloride is salted out or the base is set free by addition of alkali.

Dichlorobenzidine yields azo dyes of bluer shades than those obtained from benzidine. The fastness to acids is also much improved.

2-**Nitrobenzidine**—

$$H_2N \overset{NO_2}{\diagup}\!\!\!\diagdown \!\!\!-\!\!\!\diagup\!\!\!\diagdown NH_2$$
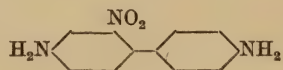
—crystallises in long red needles, m.p. 143°. The sulphate, $C_{12}H_{11}O_2N_3.H_2SO_4 + \frac{1}{2}H_2O$ is sparingly soluble in cold water, but is much more soluble than benzidine sulphate.

This nitrobenzidine is prepared by nitrating benzidine in solution in a large excess of concentrated sulphuric acid, which protects the amino groups, and at the same time directs the nitro group into the *meta* position to an amino group.

28·2 parts of benzidine sulphate are stirred into 300 parts of sulphuric acid and the mixture warmed at 50° to 60° until a clear solution is formed. The solution is cooled to 10° to 20° and 10·1 parts of potassium nitrate (nitric acid may also be used) gradually added. Stirring is continued for several hours, and the solution then poured into three times its weight of water. On cooling, nitrobenzidine sulphate crystallises out (Tauber, *Ber.*, **23**, 796; E.P. 13475 of 1892).

As previously explained (p. 32), substitution of benzidine in the 2-positions by

negative groups diminishes considerably the affinity of the derived azo dyes for cotton. This is the case with 2-nitrobenzidine, but fast wool dyes can be obtained from it, notably Anthracene Red, which is made by coupling diazotised nitrobenzidine with salicylic acid and then with NW-acid. The nitro group has a strong reddening effect on the shade, since the dye obtained from benzidine with the same two second components is brown in colour, while Anthracene Red is scarlet.

3 : 3′-Dinitrobenzidine, which can be made by nitrating diacetylbenzidine, is not used as a dyestuff intermediate.

CHAPTER III

ANILINE AND ITS DERIVATIVES

THE preparation of aniline has already been described (p. 26), and this chapter will be concerned with the intermediates derived from it.

Acetanilide—

$$NH.CO.CH_3$$
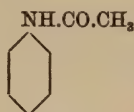
—white crystals, m.p. 112°, b.p. 304°. Very sparingly soluble in cold water, but rather more soluble in boiling water.

If aniline is boiled with one molecular proportion of glacial acetic acid, equilibrium is reached before the aniline acetate has been completely converted to acetanilide, since the water set free as the reaction proceeds dilutes the remaining acetic acid sufficiently to stop acetylation. The reaction can be pushed further towards completion by using an excess of acetic acid, but even then is not complete. If, however, the water formed is driven off, complete acetylation is obtained. Since the water cannot be driven off without carrying some acetic acid with it, the usual practice is to add such an excess of acetic acid (about 50 per cent. excess) that sufficient will be left, when all the water is driven off, to acetylate the aniline completely.

93 parts of pure aniline and 93 parts of glacial acetic acid (98 per cent. or over) are heated together in a vessel fitted with a reflux condenser. On the large scale the apparatus used is made of aluminium, which withstands the action of acetic acid very well, while iron and copper are too easily acted on. The temperature of the solution is kept at 110° for the first ten hours, then at 120° to 130° for a further ten hours, and finally at 140° to 150° for six hours. The water and excess acetic acid are then slowly distilled off, while the temperature of the melt is raised until, when the last of the water and acetic acid are passing over, it reaches about 240°. The melt is then run off into about 930 parts of water at 50° to 60°, which is being vigorously stirred. On cooling, the acetanilide is obtained mostly in granular form, the remainder having crystallised from solution in the water. The acetanilide is filtered off, dried, and powdered. The melting-point of the product is 110° to 111°, and the yield about 132 parts or 98 per cent. It can be purified by recrystallisation from a large volume of boiling water, but the crude product is sufficiently pure for its chief application— namely, its conversion to *p*-nitroaniline.

p-**Nitroaniline—**

$$NH_2$$
$$NO_2$$

—crystallises in yellow prisms, m.p. 148·3°, D 1·424. It is not volatile in steam. 1 part dissolves in 1,298 parts of water at 20°, and in 45 parts of water at 100°. 100 gms. of alcohol dissolve 5·84 gms. at 20°.

CHART III.—ANILINE AND ITS DERIVATIVES.

Aniline cannot be nitrated in the ordinary way, since oxidation products are largely formed due to the amino group being attacked. The amino group can be protected by dissolving the aniline in a large excess of concentrated sulphuric acid, but nitration in this case produces about 50 per cent. of m-nitroaniline together with substantial proportions of the o- and p-compounds. This method, therefore, is of little use for the preparation of any of the nitroanilines, though it has been successfully used for some of the nitrotoluidines (p. 118), where the predominance of one isomer is much greater.

If the amino group is protected by acylation or by condensation with an aldehyde to form a Schiff's base, nitration can then be carried out in normal fashion and the nitroaniline obtained from the nitration product by hydrolysing off the acyl or aldehyde group. Protection of the amino group is not the only advantage of this method. The nitration can be so carried out that either the para- or the ortho-nitroaniline is the main product, metanitroaniline being formed only in traces. Thus, if acetanilide, $C_6H_5.NH.CO.CH_3$, or benzylideneaniline, $C_6H_5N : CH.C_6H_5$, is nitrated in sulphuric acid solution at low temperatures, about 90 per cent. of the product is the para compound, the remainder being mostly the ortho compound. The usual method is to nitrate acetanilide.

(a) p-Nitroacetanilide.

The acetanilide, prepared as described above (132 parts), is added slowly to 530 parts of concentrated sulphuric acid, which is stirred in an iron vessel cooled externally. The temperature of the solution is kept below 30° in order to avoid hydrolysis of the acetanilide. When this is completely dissolved, the solution is cooled to 0° and 200 parts of mixed acid, composed of—

HNO_3	..	..	..	..	..	..	.. 31 per cent.
H_2SO_4	..	..	..	..	..	..	.. 47 ,,
H_2O	..	..	..	..	..	..	.. 22 ,,

—is added slowly, so that the temperature does not rise above 3°. By nitrating at this low temperature, the proportion of o-nitroaniline formed is reduced to the minimum. After the mixed acid has all been added, stirring is continued till the nitration is ended. This is recognised by precipitating a test portion in water and boiling the precipitate with dilute caustic soda, which hydrolyses the acetyl compounds, thus forming aniline from any unchanged acetanilide. Several hours are required to complete the nitration. When finished, the solution is poured on to a well-stirred mixture of 800 parts of ice and 1,600 parts of water. The nitroacetanilides are precipitated and, after an hour, filtered off and washed well with water. In order to separate the o-nitro compound from the p-, advantage is taken of the lower basicity of o-nitroaniline, which results in o-nitroacetanilide being much more easily hydrolysed than the p- isomer. The precipitate is stirred up with about 700 parts of water, made distinctly alkaline to litmus with caustic soda, and the mixture heated to boiling, when o-nitroacetanilide is quickly hydrolysed. The o-nitroaniline formed

dissolves in the alkaline water to a yellow solution. After cooling to 50°, the *p*-nitro-acetanilide is filtered off, washed alkali-free, and dried. The yield is 160 parts or about 90 per cent.

(b) *p*-Nitroaniline.

The *p*-nitroacetanilide is now boiled under a reflux condenser with 400 parts of water and about 120 parts of 35 per cent. caustic soda solution until a test portion dissolves to a clear solution in hydrochloric acid, showing hydrolysis to be complete. This requires several hours' boiling. It should be kept in mind that the vapours of the nitroanilines are poisonous. The quantity of caustic soda taken is such that the solution is only faintly alkaline at the end of the hydrolysis. The solution is now cooled and the *p*-nitroaniline, which has separated as yellow crystals, is filtered off, washed, and dried.

The yield of *p*-nitroaniline is about 100 parts (from 93 parts of aniline), an overall yield on the aniline used of about 73 per cent.

A detailed description of this process is given by P. Muller (*Chem. Ztg.*, 1912, **24,** 1055).

Another process for the preparation of *p*-nitroaniline which seems very simple and convenient is that of the Bayer patent, G.P. 72173, in which benzylideneaniline is nitrated :

$$\underset{NH_2}{\bigcirc} + OHC.C_6H_5 \longrightarrow \underset{NH_2}{\overset{N:CH.C_6H_5}{\bigcirc}} \longrightarrow \underset{NO_2}{\overset{N:CH.C_6H_5}{\bigcirc}}$$

$$\longrightarrow \underset{NO_2}{\overset{NH_2}{\bigcirc}} + C_6H_5.CHO$$
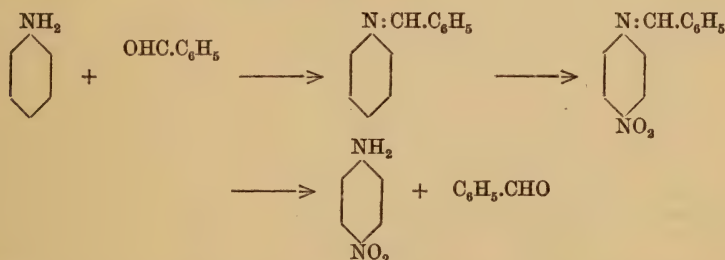
The Schiff's bases formed by condensation of aldehydes with primary amines—

$$R.NH_2 + OHC.R' \longrightarrow R.N:CH.R' + H_2O$$
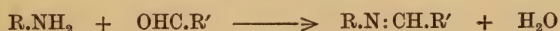
—with elimination of water, are very sensitive to dilute mineral acids, being almost immediately hydrolysed by them to the original amine and aldehyde. But they are stable in concentrated sulphuric acid of 80 per cent. strength or over. On nitration benzylideneaniline is said to give almost exclusively the *para*-nitro derivative.

Benzylideneaniline is prepared simply by mixing equimolecular proportions of benzaldehyde and aniline and warming the mixture for a short time. The water formed rises to the surface and is run off. 18·1 kg. of benzylideneaniline is run slowly with stirring into 70 kg. of 95 per cent. sulphuric acid. The temperature may be allowed to rise to 50°. The solution is then cooled to 5° and nitrated with a mixture of 10·8 kg. of 62 per cent. nitric acid and 10·8 kg. of concentrated sulphuric acid. The temperature during nitration is kept between 5° and 10°. When the nitration is ended an equal volume of water is added to the mixture, and the dilution, together

with the heat produced by it, hydrolyses the p-nitrobenzylideneaniline to p-nitroaniline and benzaldehyde. The latter is then distilled off with steam, nearly all the benzaldehyde being recovered and used again. On cooling the residual liquid and diluting further with water, the p-nitroaniline separates. The separation can be completed by nearly neutralising the acid. The p-nitroaniline so obtained is claimed to be pure. On crystallising from alcohol, all the fractions obtained show the same melting-point of 148°. The yield is over 90 per cent.

A third process for the preparation of p-nitroaniline is described on p. 8.

p-Nitroaniline is used as a first component in azo dyes. In some cases, after coupling diazotised p-nitroaniline with a second component, the nitro group is reduced by means of sodium sulphide, which does not affect the azo group. The aminoazo compound thus formed is then, either diazotised and coupled with a third component, or phosgenated to give a diphenylurea derivative :

$$R.N:N.C_6H_4.NO_2 \longrightarrow R.N:N.C_6H_4.NH_2 \begin{cases} R.N:N.C_6H_4.N_2Cl \\ R.N:N.C_6H_4.NH \\ \qquad\qquad\qquad CO \\ R.N:N.C_6H_4.NH \end{cases}$$
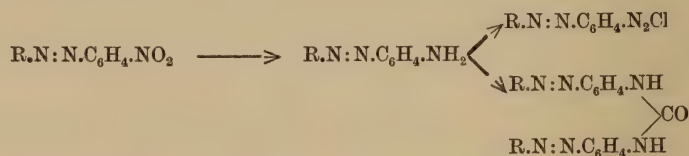
p-Nitroacetanilide can be reduced to p-aminoacetanilide :
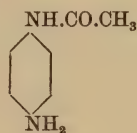
It crystallises in colourless needles when pure, but these soon turn brown. M.p. 162° to 162·5°. It is sparingly soluble in cold and moderately in hot water, but easily soluble in alcohol and ether. It gives stable well-crystallised salts with mineral acids.

The reduction by the ordinary method is apt to be accompanied by some hydrolysis yielding a product containing some p-phenylenediamine, but this can be avoided by using acetic acid instead of hydrochloric acid and taking about 2 per cent. of the theoretical quantity (see Reduction of Nitrobenzene, p. 26), so that the reduction is carried out under practically neutral conditions (Nietzki, *Ber.*, **17**, 343).

The nitroacetanilide (about 160 parts), prepared from 93 parts of aniline, is added slowly to a boiling mixture of 250 parts of cast-iron borings, 500 parts of water, and 15 parts of 40 per cent. acetic acid in an iron pot. Reduction takes place quickly, and the liquid spotted on filter-paper should be colourless. Boiling is continued for a few minutes after all the nitro compound has been added, the volume being maintained by addition of water. The iron in solution cannot be precipitated at the boil in this case, for fear of hydrolysis. The solution is cooled to 70°, made alkaline with soda, which precipitates most of the dissolved iron, and the remainder precipitated by careful addition of ammonium sulphide solution. The mixture is filtered and the filtrate concentrated to the crystallising point, when on cooling the p-aminoacetanilide

separates as brown needles. It can be purified by recrystallisation from water containing some animal charcoal.

p-Aminoacetanilide serves to some extent the same purposes as *p*-nitroaniline. That is, its diazo compound is coupled with an amine or phenol, and on hydrolysing the acetylaminoazo compound so formed, the amino group set free may be diazotised and coupled with a fresh component, or may be phosgenated.

p-Phenylenediamine :

$$NH_2$$

$$NH_2$$

The base forms white crystals, m.p. 147°, b.p. 267°, but quickly turns brown, and finally black in air. The salts are more stable.

p-Phenylenediamine may be prepared by hydrolysis of *p*-aminoacetanilide with acids or alkalies. Naturally, acids are preferable for the purpose, as the base is so easily oxidised. Again, *p*-nitroacetanilide may be reduced under acid conditions, so that hydrolysis accompanies reduction. Finally, *p*-nitroaniline yields the diamine on reduction. The use of this last method on a technical scale is described by Jansen (*Zeit. f. Farben-Industrie*, 1913, **12**, 197).

A mixture of 200 kg. of ground iron borings, 9 litres of 28 per cent. hydrochloric acid and water, is boiled and stirred in an iron vessel, and 200 kg. of *p*-nitroaniline slowly added. The violent reaction with frothing which takes place on each addition of the nitroaniline is allowed to subside before the next addition. Water is also slowly dropped in to maintain the volume. When all the nitroaniline has been added the liquid is yellow in colour. Reduction is completed by adding 14 litres of 28 per cent. hydrochloric acid and stirring further until a drop of the solution gives a colourless spot on filter-paper. The solution is now made faintly alkaline to phenolphthaleïn by the addition of soda ash (about 25 kg.), and after boiling up for ten minutes is allowed to settle and filtered, the iron residues being well washed out with hot water. The solution is then concentrated to the crystallising point, when on cooling the diamine separates out as a hydrate. The yield is said to be 90 to 95 per cent. and the product very pure.

The practice of precipitating the dissolved iron by making alkaline and thus setting free the base does not seem desirable in the case of *p*-phenylenediamine. The method of G.P. 269542 previously described in connection with *m*-phenylenediamine (p. 21) can be adopted in this case to obtain white crystals of the hydrochloride. 100 gms. of *p*-nitroaniline are reduced with 730 c.c. of 30 per cent. hydrochloric acid and 150 gms. of iron as described in the case of *m*-phenylenediamine.

p-Phenylenediamine base can only be obtained in a satisfactorily pure state by vacuum distillation.

Reduction of aminoazobenzene also yields *p*-phenylenediamine.

p-Phenylenediamine cannot be used as an intermediate for azo dyes. On attempting to diazotise it a mixture of oxidation products, partly of a quinonoid nature, is

formed. This difficulty is overcome by forming first a monoazo compound by means of either p-nitroaniline or p-aminoacetanilide and then reducing with sodium sulphide or hydrolysing, when the newly-formed amino group may be diazotised and coupled with a second component. The ready oxidisability of the base, however, makes it specially suitable for dyeing hair and furs. It is also used for sulphide dyes.

The Alkylation of Aniline.

The alkylanilines have long occupied an important position as intermediates for dyestuffs, owing to the large number of brilliant basic dyes of the triphenylmethane and other classes which can be prepared from them. The tertiary amines—dimethyl- and diethylaniline, together with benzylmethyl- and benzylethylaniline—are of greatest importance, but subsidiary uses have also been found for the secondary amine, mono-ethylaniline.

Two general methods are in use for the alkylation of aniline. The first (and newer) method uses the alkyl chloride :

$$C_6H_5.NH_2 \ + \ R.Cl \ \longrightarrow \ C_6H_5.NHR \ + \ HCl$$
$$C_6H_5.NH_2 \ + \ 2R.Cl \ \longrightarrow \ C_6H_5.NR_2 \ + \ 2HCl$$
$$(R=CH_3, C_2H_5, C_6H_5.CH_2)$$
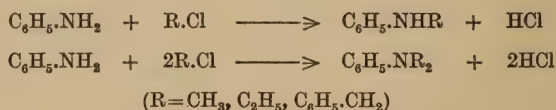
By this method, the alkylation may be carried out at moderate temperatures (100° or under) and under moderate pressures, or, in the case of benzyl chloride, at atmospheric pressure. Sufficient alkali (sodium carbonate, caustic soda, or lime) is added to neutralise the hydrochloric acid formed.

The second (older method) consists in heating aniline with the appropriate alcohol in presence of a condensing agent :

$$C_6H_5.NH_2 \ + \ R.OH \ \longrightarrow \ C_6H_5.NHR \ + \ H_2O$$
$$C_6H_5.NH_2 \ + \ 2R.OH \ \longrightarrow \ C_6H_5.NR_2 \ + \ 2H_2O$$
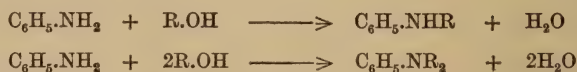
Although water is eliminated in the reaction, experience shows that dehydrating agents do not, as such, facilitate alkylation. For instance, aniline, ethyl alcohol, and quicklime may be heated together to a high temperature without any formation of ethylanilines. The best condensing agents are acids, in particular sulphuric and hydrochloric acids, so that this second method is probably identical with the first, alkyl chloride or sulphate being formed from the alcohol and acid, followed by alkylation of the aniline with regeneration of the acid.

Knoevenagel (*J. pr. Chem.*, 1914, **89**, 31) found that traces of iodine accelerate the reaction between aniline and alcohols in a remarkable degree. The method has been patented by Knoll and Co. (G.P. 250236), who claim to obtain quantitative yields of dimethyl- and diethylaniline in this way. For example, 93 parts of aniline, 96 parts of methyl alcohol, and 1 part of iodine, are heated in an autoclave at 230° for seven hours. The water is separated, the iodine removed by alkali, and the product distilled in a vacuum. With ethyl alcohol, the temperature used is 235° and the time

of heating ten hours. Confirmation of these results is lacking, and the process apparently is not used technically.

The side reactions which are liable to occur in the ordinary alkylation process are of two kinds :

      1. The formation of quaternary ammonium salts.
      2. The formation of nuclear alkyl derivatives.

Quaternary ammonium salts, *e.g.*—

$$C_6H_5.N \underset{\underset{HSO_4}{|}}{\overset{\nearrow CH_3}{\underset{\searrow CH_3}{-CH_3}}}$$
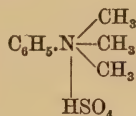
—are particularly apt to form when sulphuric acid is used as condensing agent. They are very stable, and are not decomposed by alkalies at ordinary temperatures, but merely yield the corresponding substituted ammonium hydroxide bases, *e.g.*—

$$C_6H_5.N \underset{\underset{OH}{|}}{\overset{\nearrow CH_3}{\underset{\searrow CH_3}{-CH_3}}}$$
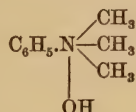
—which are reconverted to the ammonium salts by acids. They are also soluble in water and non-volatile in steam, so that they remain behind in the alkaline liquor in the usual separation of the secondary and tertiary bases. However, they may be decomposed, and the tertiary bases recovered, by heating with concentrated caustic alkali at about 170° to 180°.

The second side reaction—the formation of nuclear derivatives—is apparently a consequence of the first. Above a certain temperature limit which, for the bases of the benzene series, is about 250° to 300°, quaternary ammonium salts undergo intramolecular transformation, an alkyl group being detached from the nitrogen atom and entering the nucleus in the para position :

Since, however, alkylation can be carried to completion at 230° or under, no nuclear derivatives need be obtained unless serious local overheating has occurred during the process.

Methylaniline—

—colourless oil, b.p. 195·7° (765 mm.), 95° (25 mm.); D_{15}^{15} 0·9921.

Methylaniline is formed when aniline is heated with methyl alcohol and a little sulphuric acid in an autoclave at 180° to 200°, or when aniline hydrochloride is heated with methyl alcohol at the same temperature. But the resulting products contain substantial proportions of unchanged aniline and dimethylaniline, whose separation is troublesome.

A special method has been devised for the preparation of methylaniline depending on the use of formaldehyde. This method was first applied in the Geigy patent, G.P. 75854. Aniline is mixed with an equimolecular proportion of aqueous form-aldehyde and caustic soda. A clear solution is formed at first, but this soon warms up, becomes cloudy, and a heavy oil separates. The whole liquid is now stirred rapidly and zinc dust added. While heating at 70° to 90°, a further quantity of caustic soda solution is slowly added until a test portion of the liquid dissolves, apart from the zinc, to a clear solution in acetic acid. The methylaniline formed is separated by steam distillation. The yields by this process are very poor.

The reaction between formaldehyde and aniline is somewhat complex. A Schiff base, $C_6H_5.N:CH_2$, is first formed, but this quickly polymerises to oily products, and finally to a white solid of unknown constitution whose composition corresponds to the formula $(C_6H_5.N:CH_2)_3$. There is also the possibility of formation of methylene-dianiline, $C_6H_5.NH.CH_2.NH.C_6H_5$. The heavy oil mentioned in the Geigy patent probably contains all of the above products. It is, however, only the unstable Schiff base which can be reduced to methylaniline :

$$C_6H_5.N:CH_2 \ + \ 2H \ \longrightarrow \ C_6H_5.NHCH_3$$
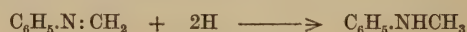
If time is given for the Schiff base to polymerise, the yield of methylaniline will be correspondingly reduced.

With these facts in view, a more recent patent by G. T. Morgan (E.P. 102834) proposes an improved method in which the Schiff base is reduced as soon as it is formed.

A mixture of 300 parts of water and 200 parts of 34 per cent. caustic soda solution (D 1·37) containing 90 parts of zinc dust in suspension is stirred thoroughly and heated to 90°. To this are added separately and concurrently at equivalent rates 60 parts of aniline and 66 parts of 40 per cent. formalin, so that the addition takes about two hours. Stirring and heating are then continued for a further six hours, while 40 parts more formalin are slowly added. Samples are taken from time to time and tested for methylaniline, until the proportion of this reaches a maximum. The methylaniline is then separated from the mixture by distillation in steam. It is advantageous to activate the zinc by addition of a little copper sulphate or other copper salt to the mixture at the beginning.

Methylaniline is not used as a dyestuff intermediate, but is converted into two tertiary amines, benzylmethylaniline and ethylmethylaniline, which are used to some extent for triphenylmethane colours.

Dimethylaniline—
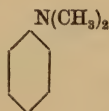
—colourless oil, b.p. 193° (760 mm.), 103° (34 mm.). D_4^{20} 0·9575. It is almost insoluble in water, but is miscible with most organic liquids. It is volatile in steam.

This is by far the most widely used of the alkylanilines, probably because it is the most easily prepared in good purity and yield. The usual method of preparation is to heat aniline with methyl alcohol and a little sulphuric acid. A long account, with many details of plant, is given of this process by Walter (*Chem. Ztg.*, 1910, **34,** 641, 667, 681, 690).

80 kg. of pure aniline, 78 kg. of methyl alcohol (free from acetone and ethyl alcohol—*i.e.*, it must not give a positive iodoform test) and 8 kg. of concentrated sulphuric acid are mixed in an autoclave and heated to about 215° for nine hours. The pressure reaches about 30 atmospheres when the full temperature is attained, but later falls slightly. After allowing the autoclave to cool to about 100°, the outlet valve is opened and the issuing gases, methyl alcohol and methyl ether, led through a condenser, where the alcohol is condensed, the methyl ether, which is gaseous at ordinary temperature, passing on through a long column of water. The autoclave contents are then transferred to a still, made alkaline with caustic soda, and the dimethylaniline distilled in steam. The separated dimethylaniline is then distilled. The yield obtained is 98 kg. or 94 per cent. of the theoretical.

Somewhat greater yields may be obtained by taking account of the fact that some quaternary ammonium sulphate (p. 43) is formed during methylation. This can be decomposed, with regeneration of dimethylaniline and methyl alcohol, by making the autoclave contents alkaline with caustic soda and heating again to 170° for several hours. After cooling the procedure is the same as before.

The usual impurities of the crude product are aniline and methylaniline. Neither should be present in quantity with reasonably careful working. Any aniline present can be separated during distillation of the product. The presence of methylaniline is shown by adding acetic anhydride to a sample, when acetylation of the methylaniline takes place with rise of temperature. Pure dimethylaniline gives a slight lowering of temperature on mixing with acetic anhydride. The test may be used as a rough method of estimation for small proportions of methylaniline in dimethylaniline. 5 c.c. of the liquid are mixed with 5 c.c. of acetic anhydride at the same temperature, and the rise of temperature noted. Each degree of rise is equivalent to about 0·5 per cent. of methylaniline. Usually not more than about 0·5 per cent. of methylaniline is present, as indicated by this test.

Methylation of aniline with methyl chloride is described by Grandmougin (*Rev. Prod. Chim.*, 1917, **20,** 68). This process has the great advantage that low-pressure vessels and moderate temperatures may be used. 50 kg. of aniline is mixed with 75 litres of milk of lime made from 40 kg. of quicklime, and the mixture heated to 100° with continuous stirring. Methyl chloride is then forced in at such a rate that the pressure is maintained at 5 to 6 atmospheres. 62 kg. of methyl chloride is added in all, and the addition takes about two hours. Heating and stirring are continued till methylation is complete, as shown by a fall in the pressure to $2\frac{1}{2}$ atmospheres. The dimethylaniline is then distilled with steam and purified as usual.

Some work of an inconclusive character has been published regarding the effect of dimethyl sulphate on aniline (Ullmann, *Ann.*, 1903, **327**, 104; Werner, *J.C.S.*, 1914, **105**, 2762; Shepard, *J. Am. Chem. Soc.*, 1916, **38**, 2507), but a satisfactory method of preparing dimethylaniline by the use of this methylating agent does not seem to have been worked out. Probably the tendency to form quaternary ammonium salts is too great in this case.

The Ethylanilines.

Unlike the methylation of aniline, ethylation cannot be conveniently carried completely to diethylaniline, nor can ethylaniline be obtained alone by any process. Mixtures of the two are always obtained. They will, therefore, be described together.

Ethylaniline—

NHC_2H_5
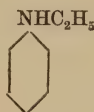
—colourless oil, b.p. 204°, D_{15}^{15} 0·9643.

Diethylaniline—

$N(C_2H_5)_2$
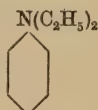
—colourless oil, b.p. 214°, D_{15}^{15} 0·9388.

Ethylation of aniline can be carried out by means of ethyl alcohol, but in this case sulphuric acid cannot be used as condensing agent owing to the large amount of ether formed. Hydrochloric acid is usually employed instead, aniline hydrochloride ("aniline salt") being heated with alcohol. Unfortunately, this necessitates the use of enamelled autoclaves.

If aniline hydrochloride and ethyl alcohol in equimolecular proportions are heated at 180° for twelve hours, a mixture containing about 70 per cent. of ethylaniline, some diethylaniline, and unchanged aniline is formed, from which on cooling the ethylaniline mostly separates as hydrochloride. If 25 per cent. excess of alcohol over the molecular proportion is used, and the temperature raised to 190° (the pressure developed is 16 atmospheres), the aniline is completely ethylated. The oil obtained on making alkaline and distilling in steam as usual then contains about 23 per cent. diethylaniline and 77 per cent. monoethylaniline.

The acetic anhydride method for estimating the proportion of secondary amine is not sufficiently accurate for use with such mixtures. It is only of use where the proportion of secondary amine is small. But in the case of the ethylanilines an accurate determination of the specific gravity of the mixture at 15° will give the required information (if aniline is absent) when used in conjunction with the table given on p. 47 (Fierz-David, "Farbenchemie," second edition, 1923, p. 110).

As there is a difference in boiling-point of 10° between mono- and diethylaniline it is possible to separate them by repeated fractional distillation, using long columns. But this is not usually done. Instead, the mixture is benzylated, as described later

Specific Gravity.	Diethyl (per Cent.).	Specific Gravity.	Diethyl (per Cent.).	Specific Gravity.	Diethyl (per Cent.).	Specific Gravity.	Diethyl (per Cent.).
0·9646	0	0·9610	15·0	0·9545	41·0	0·9430	85·0
0·9643	1	0·9595	21·2	0·9520	50·8	0·9415	90·2
0·9640	2·3	0·9585	25·3	0·9495	60·4	0·9400	95·6
0·9637	3·7	0·9570	31·2	0·9470	70·0	0·93875	100
0·9622	9·8	0·9560	35·2	0·9440	81·3	—	—

(p. 49), and the benzylethylaniline and diethylaniline are then more easily separated. The proportion of diethylaniline in the mixture can be increased by increasing the alcohol used.

If hydrobromic acid is substituted for hydrochloric acid, ethylation can proceed at a much lower temperature, yielding much higher proportions of tertiary amine. Städel (*Ber.*, 1883, **16**, 30; G.P. 21241), by heating aniline hydrobromide with 2·2 mols. of ethyl alcohol at 145° to 150°, claimed to obtain a nearly quantitative yield of diethylaniline. The method, however, apparently has not been adopted on a manufacturing scale. Hydrobromic acid is, of course, much more costly than hydrochloric, and in any case the benzylethylaniline produced in the ordinary process is a valuable intermediate for triphenylmethane colours.

A detailed laboratory investigation of the ethylation of aniline hydrochloride by ethyl alcohol, more particularly with regard to the use of catalysts, has been made by Johnson, Hill, and Donleavy (*J. Ind. Eng. Chem.*, 1920, **12**, 636). They found that zinc chloride, or calcium chloride, and the bromides and iodides of sodium and potassium gave increased yields of ethylated aniline, and also that cupric chloride specially favoured the production of diethylaniline. The effect was further increased by using cupric chloride in conjunction with one of each of the other two classes of catalysts. The conditions giving the highest yield of diethylaniline were as follows. The autoclave was charged with :

Aniline hydrochloride	100 gms.
Ethyl alcohol (99 per cent.)	360 ,,
Sodium bromide	10 ,,
Calcium chloride	10 ,,
Cupric chloride	5 ,,

The charge was heated at 175° to 180° for eight hours, the pressure developed being 280 to 310 lbs. per square inch. Under these conditions consistent yields of 100 to 105 gms. of diethylaniline, containing about 5 per cent. of monoethylaniline, were obtained. This corresponds to a yield of 87 to 91 per cent.

As regards other ethylating agents for aniline, ethyl chloride is available in quantity, and, like methyl chloride, has the advantage of requiring for use low-pressure iron vessels at temperatures not above 100°. But details are lacking of the results obtainable by its use.

Applications of the Alkylanilines.

The chief use of the alkylanilines as dyestuff intermediates depends on their readiness to condense with aldehydes as follows :

$$R.CHO + 2C_6H_5.NR'_2 \longrightarrow R.CH \begin{cases} NR'_2 \\ NR'_2 \end{cases}$$
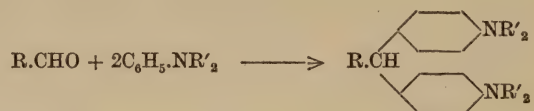
If benzaldehyde or its derivatives are used, the condensation products are the *leuco* bases of triphenylmethane dyes, from which the dyes themselves are obtained by oxidation. In this way from benzaldehyde itself and dimethyl- and diethylanilines are obtained Malachite Green and Brilliant Green respectively. Others are obtained by using sulpho-, chloro-, and hydroxy- derivatives of benzaldehyde.

Formaldehyde also condenses with the alkylanilines, yielding diphenylmethane derivatives (" Methane Base," etc.), which will be dealt with later.

The dialkylanilines, on treatment with nitrous acid, give *p*-nitroso derivatives, which are used in the preparation of azine, thiazines, and oxazine colours. But the dialkylanilines are used directly in making these colours. By oxidising in faintly acid solution a mixture of a dialkylaniline and a *p*-aminodialkylaniline, an indamine is formed :

This indamine may be further condensed with aniline or another aromatic amine to form an azine dye :
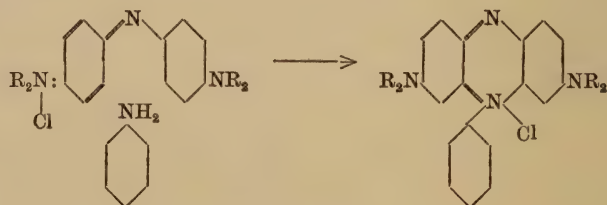
The indamine may also be formed by condensation of a *p*-nitrosodialkylaniline with a dialkylaniline :
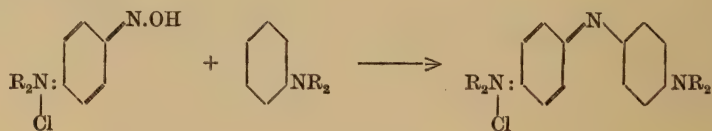
By using a nitroso compound containing a hydroxyl group in the *ortho* position to the nitroso group, the indamine which is first formed condenses further to an oxazine :

Thiazines are formed by introducing the group —$S.SO_3H$ in the *ortho* position to the amino group of *p*-aminodialkylanilines, which are then condensed, by oxidation with dialkylanilines, to indamines, and further to the thiazines. Details of these methods are to be found in works on the chemistry of dyestuffs. They are mentioned here merely to indicate the various modes of application of the dialkylanilines.

A subsidiary use of dimethylaniline is its application as a second component in a few azo dyes, which are chiefly of use as indicators.

Benzylmethylaniline—
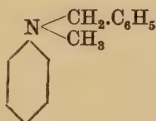
—pale yellow oil, b.p. 305° to 306° or 210° (60 mm.).

Benzylethylaniline—
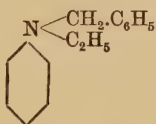
—pale yellow oil, b.p. 285° to 286° (710 mm.) or 185·5 to 186·5° (22 mm.). $D^{18·5}$ 1·034.

Although the two benzylalkylanilines are intermediates of importance for acid colours of the triphenylmethane series, but little information has been published regarding them. The preparation of the methyl compound has been described by Wedekind (*Ber.*, 1899, **32,** 519) and that of the ethyl compound by Stebbins (*J. Am. Chem. Soc.*, 1885, **7,** 42), in each case by heating the monoalkylaniline with benzyl chloride and then fractionating the product. But good results are not obtained in this way. In order to obtain approximately complete benzylation it is advisable to have present sufficient aqueous alkali to neutralise the hydrochloric acid formed.

As already mentioned, the monoalkylanilines are not used as dyestuff intermediates. Since, however, they are present in the products of alkylation of aniline, and especially in the case of ethylated aniline, it is found most economical to benzylate the mixtures of secondary and tertiary bases. This is carried out by determining the proportion of secondary base in the mixture, adding the calculated quantity of benzyl chloride, together with about 5 per cent. excess, and the necessary aqueous solution of alkali (caustic soda or sodium carbonate), and heating the mixture at 100° to 125°. In the case of the higher temperatures closed vessels must be used. In any case the

mixture must be very vigorously stirred.   When benzylation is finished the dimethyl-
or diethylaniline is distilled off with steam and purified in the usual way.   The re-
maining benzylalkylaniline, which is not volatile in steam, is then separated, washed,
and purified by fractional distillation under reduced pressure.   The forerunnings
contain some benzyl alcohol (b.p. 206°) formed by partial hydrolysis of the benzyl
chloride.

The benzylalkylanilines react in the same way as dimethyl- and diethylaniline
with benzaldehyde and its derivatives to yield the *leuco* bases of triphenylmethane
dyes of slightly bluer shades than those obtained from the diethyl compound.   The
benzyl compounds are specially well adapted for the production of **acid** colours for
wool and silk, since they are easily sulphonated at temperatures not much above the
ordinary.   The sulphonation may either be performed on the benzyl compound itself
or on the *leuco* triphenylmethane base made from it.   In either case, the sulphonic
acid group enters the benzyl nucleus first, in the *para* position.   Thus, for example,
benzylethylanilinesulphonic acid—

$$\langle\ \rangle N(C_2H_5).CH_2\langle\ \rangle SO_3H$$
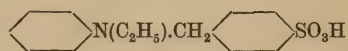
—is prepared according to G.P. 50782 (A.G.F.A.) by stirring 50 kg. of benzylethyl-
aniline into 120 kg. of 21 per cent. oleum at 40° to 50° and keeping the solution at
this temperature until a sample is soluble in dilute caustic soda.   The acid is then
separated simply by diluting the solution with 100 kg. of water, so that the tempera-
ture does not rise above 50°, or, keeping under the same temperature limit, by adding
100 kg. of 40 per cent. caustic soda.

The sulphonation can also be carried out with monohydrate at 110° to 120°.

A disulphonic acid can also be obtained, in which the second sulpho group enters
the other nucleus.   **Benzylethylanilinedisulphonic acid :**

$$\langle\ \rangle N(C_2H_5).CH_2\langle\ \rangle SO_3H$$
$$HO_3S$$
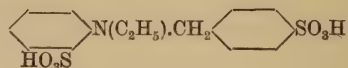
10 kg. of benzylethylaniline are stirred into 20 kg. of 20 per cent. oleum, which is
well cooled.   When solution is complete, 25 kg. of 80 per cent. oleum are added, and
the solution heated at 60° until disulphonation is complete, as shown by a test portion,
diluted with water and partly neutralised by soda, no longer giving a precipitate of
sulphonate salted out by sulphate.   The melt is then poured into water, neutralised
with milk of lime, filtered from calcium sulphate, and the calcium salt converted to
the sodium salt by sodium carbonate.   The sodium salt is then salted out (G.P. 69777,
Bayer).

The benzylalkylanilines can be condensed with aromatic aldehydes, in the same
way as the dialkylanilines, to form the *leuco* bases of triphenylmethane dyes.   The
dyes obtained on oxidation are, like those formed from the dialkylanilines, basic in
character.   As basic dyes they show no advantage over their alkyl analogues.   But
the presence of the benzyl groups enables sulphonation of the dyestuffs to take place
easily, the sulpho groups entering the benzyl nuclei, and acid dyes for wool and silk are

thus obtained, which at the same time retain all the brilliance of the basic triphenyl-methane dyes. The same dyes may also be formed by using the sulphonic acid derivatives of the benzylalkylanilines.

p-**Nitrosodimethylaniline hydrochloride :**
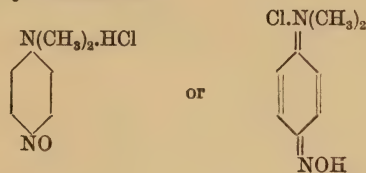
The base forms dark green leaflets when crystallised from benzene or carbon tetra-chloride. M.p. 85°. It gradually decomposes on standing, going brown. This decomposition is said to be prevented by addition of a little sodium carbonate. The hydrochloride forms intensely yellow needles, moderately soluble in water, but sparingly soluble in dilute hydrochloric acid, and in methyl and ethyl alcohols. The hydrochloride is also unstable as usually prepared, though if pure it may be kept for months.

121 gms. of dimethylaniline are dissolved in 300 c.c. of concentrated hydrochloric acid, and about 1,000 gms. of ice added. The mixture is stirred rapidly and a saturated solution of 75 gms. of sodium nitrite in water (about 200 c.c. are required) is added slowly from a tap-funnel whose end dips beneath the surface, until free nitrous acid can be detected by the smell. The usual starch-iodide paper test cannot be used in this case, because the nitroso compound itself reacts with the iodide. The temperature is maintained at or near 0°, if necessary by means of more ice. An intense orange solution is at first formed from which the hydrochloride soon begins to crystallise out. Stirring is continued for a few hours after the nitrite has been added. The hydro-chloride is then filtered off, washed with a little 10 per cent. hydrochloric acid, and air-dried. If a second wash with alcohol is given, the nitroso compound will keep much better. It is, however, usually prepared as required on the large scale, and used immediately without drying. The content of the moist substance in nitroso compound is estimated by reduction of a weighed quantity in dilute acid solution with zinc dust to *p*-aminodimethylaniline, followed by titration with nitrite.

p-**Nitrosodiethylaniline hydrochloride** is prepared in a similar way, but its solu-bility is too great to allow of the dilution used in the preceding case. The solution of diethylaniline in concentrated hydrochloric acid is cooled externally by a freezing mixture, while the nitrite is run in.

As already mentioned (p. 48), the *p*-nitrosodialkylanilines can be condensed with dialkylanilines to form indamines, which can be further condensed to azine, oxazine, or thiazine dyes. In such cases there is always the alternative method of using a *p*-aminodialkylaniline, a mixture of this with a dialkylaniline being oxidised to form the indamine. However, the *p*-aminodialkylaniline is generally most conveniently obtained by reduction of the nitroso compound, and, except in special cases, there is no advantage in the use of the amino compound.

A large number of azine and oxazine dyes are formed by condensation of these
p-nitroso compounds with *m*-diamines or substituted *m*-diamines, and with phenols :
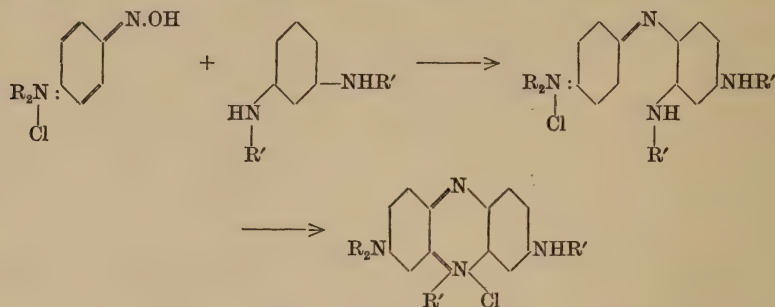
As phenols, resorcinol, β-naphthol, gallic acid, dialkyl-*m*-amino-phenols and -cresols
are specially well adapted for this reaction.

Tetramethyldiaminodiphenylmethane (Methane Base)—
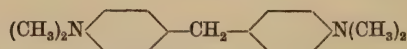
—colourless lustrous leaflets, m.p. 90° to 91°.   Insoluble in water, sparingly soluble
in cold alcohol, but much more so in hot alcohol, and in ether and benzene.   It is
not volatile in steam, and may be distilled undecomposed.   B.p. 390°.

This substance is made by condensation of formaldehyde with dimethylaniline.
The reaction apparently takes the following course :
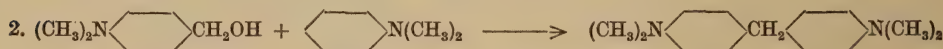
If a considerable excess of formaldehyde is used, higher condensation products of
unknown constitution are formed.   This was the chief fault of the early methods of
preparation, together with the use of organic solvents such as alcohol or acetic acid.
The following method is due in essentials to Cohn (*Chem. Ztg.*, 1900, **24,** 564): 242 gms.
(2 mols.) of pure dimethylaniline are mixed with 300 gms. of 25 per cent. hydrochloric
acid (just enough to hold the dimethylaniline in solution) and 90 gms. of 40 per cent.
formaldehyde (1·1 mols.) added.   The strength of the formaldehyde solution should
be accurately known.   The mixture is then heated on the water-bath at about 85°,
with occasional stirring, for five hours.   After cooling, the base is separated by making
just alkaline with ammonia or sodium carbonate solution.   It is filtered off, thoroughly
washed with water, and dried at about 60°.   The yield is practically quantitative,
about 255 gms.   It may be purified by recrystallisation from alcohol.

Tetraethyldiaminodiphenylmethane is prepared in the same way from diethyl-
aniline.

Methane base is used in making Auramine by first converting the —CH₂— group

into —C : S by heating with sulphur, and then condensing this with ammonia (from ammonium chloride) to form the imino compound —C : NH.

Tetramethyldiaminobenzophenone (Michler's Ketone)

$$(CH_3)_2N \bigodot CO \bigodot N(CH_3)_2$$

—silver-glancing leaflets.   The melting-point was given by Michler as 179°, but later work points to the figure 172° to 172·5°.   Easily soluble in alcohol and ether.

The preparation is given by Michler (*Ber.*, 1876, **9**, 716, 1900).   Phosgene is passed into 100 gms. of freshly distilled dimethylaniline at ordinary temperature in an autoclave until 41 gms. have been added.   This converts about half the dimethylaniline into *p*-dimethylaminobenzoylchloride $(CH_3)_2N.C_6H_4.CO.Cl$, which partly separates as a crystalline mass.   The autoclave is then closed and heated for five hours in boiling water.   After cooling, any unchanged dimethylaniline is distilled off with steam, and the residue is dissolved in dilute hydrochloric acid.   The solution is filtered and the ketone precipitated by addition of caustic soda.   The crude ketone is filtered off, redissolved in dilute hydrochloric acid, and reprecipitated by caustic soda. It separates as a light flocculent precipitate, which is filtered off, washed, and dried. It is then recrystallised from alcohol and the crystals washed with a little cold alcohol.

Tetramethyldiaminobenzhydrol (Michler's Hydrol)—

$$(CH_3)_2N \bigodot CH(OH) \bigodot N(CH_3)_2$$

—prismatic crystals from benzene or ether.   M.p. 96°.   Soluble in alcohol.   It forms a hydrochloride, $C_{17}H_{22}ON_2.HCl$, which is very soluble in alcohol, but is hydrolysed by water.

This substance can be prepared either by oxidation of methane base or by reduction of Michler's ketone.   The former is the cheaper method, and is the one used technically, though the product obtained is rather impure.   The latter method gives an almost pure product.   Both methods are described by Möhlau and Heinze (*Ber.*, 1902, **35**, 359, 360).

1. **Oxidation of Methane Base.**—20 gms. of pure methane base are brought into solution by 50 gms. of water and 5·7 gms. of HCl as concentrated hydrochloric acid (2 mols.).   The solution is then diluted with 1,600 c.c. of water and 9·4 gms. (2 mols.) of glacial acetic acid added.   The whole is cooled below 0°, stirred vigorously, and a thin paste of lead peroxide containing 18·8 gms. of PbO_2 run in as a thin stream. The strength of the lead peroxide paste must be accurately determined beforehand by one of the usual methods.   The oxidation is quickly completed.   After five minutes a solution of 26 gms. of Glauber salt in 120 gms. of water is added to precipitate the lead as sulphate.   This is filtered off.   To the filtrate, which is an intense blue-violet in colour, excess of cold dilute caustic soda is added.   The hydrol separates as a grey flocculent precipitate, or sometimes in a soft sticky condition.   In the latter case, the whole is allowed to stand for some hours, when the precipitate hardens.   It is filtered off, washed, and dried.   The yield of crude product is 20 gms. or 94·3 per cent.

It is, however, not pure, its melting-point being about 87°. On digesting it with cold ether, about nine-tenths of it is dissolved, and on evaporating off the ether fairly pure hydrol is obtained, melting at 96° to 98°. The undissolved tenth melts at 103° to 104°, and consists mostly of an anhydride of the hydrol.

2. **Reduction of Michler's Ketone.**—26·8 gms. of the ketone is added to 1·5 litres of 95 per cent. alcohol, and the solution boiled on the water-bath. 160 gms. of 3 per cent. sodium amalgam is added to the solution, which is kept gently boiling. The reduction takes three to four hours, the end being recognised by the mobility of the residual mercury when the amalgam has been used up. The solution is then filtered, and the hydrol precipitated by running the solution into water. It is filtered off and washed with water. As so obtained it melts at 95° to 96°. The yield is quantitative.

Michler's ketone and hydrol make possible an extension of the synthesis of tri-phenylmethane colours to cases where the aldehydes required by the other chief synthetic method are not available. They can be condensed with a large variety of aromatic derivatives, including bases (primary, secondary, and tertiary), phenols and phenolic acids, and the corresponding naphthalene derivatives, to form triphenyl-methanes and diphenylnaphthylmethanes. Condensation generally takes place in the para position to the amino or hydroxyl group, though in the case of β-naphthol derivatives it takes place in the α-position.

Michler's ketone is generally employed in the form of its dichloride, formed by heating the ketone with phosphorus trichloride or oxychloride, or with phosgene.

For some cases, either the ketochloride or the hydrol may be used, but in other cases one of the methods gives better results than the other. No general rule can be laid down as to which should be used in a given case.

Alkylated *m*-Aminophenols.

These intermediates, which are required for the Pyronine and Rhodamine dyes, are usually prepared from the alkylanilines by sulphonation and alkali fusion of the sulphonates, though other methods are available. Very little exact information has been published with regard to their preparation. The sulphonation of the alkyl-anilines yields mixtures of the *m*- and *p*-sulphonic acids, the *m*-compounds being favoured by low temperature of sulphonation. No attempt is made to separate the two acids. On fusion of the sulphonates with alkali, the *p*-sulphonates are un-attacked under such conditions as give the *m*-phenols.

Dimethyl-*m*-aminophenol—

$$N(CH_3)_2$$

$$OH$$
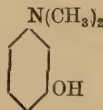
—crystallises from ligroin or benzene in needles, m.p. 87°, b.p. 265° to 268° (760 mm.), b.p. 133° (15 mm.). It is almost insoluble in water, but easily soluble in alcohol, ether, benzene, and acetone. It dissolves in acids and alkalies, and is precipitated from

alkaline solution by carbon dioxide or acetic acid, or from mineral acid solution by sodium carbonate or acetate.

The preparation of this substance is given in G.P. 44792 (*Soc. Chem. Ind.*, Basle), but the same process is described in rather more detail by Möhlau and Bucherer ("Farbenchemisches Praktikum," 1908, pp. 30, 44) as follows : Dimethylaniline (100 gms.) is slowly dropped into 650 gms. of 30 per cent. oleum, which is well stirred in an enamelled sulphonation pot externally cooled with salt and ice. The temperature is kept below 5° during the addition. The solution is warmed to 60°, and kept at this temperature until a sample dissolves clear in excess caustic soda solution. The solution is then stirred into 3 litres of water, neutralised with milk of lime, filtered from gypsum, the requisite amount of potassium carbonate added to the filtrate, the hot solution of potassium salt filtered from chalk and evaporated to dryness.

For the fusion, 200 gms. of caustic potash and 25 c.c. of water are melted in a nickel vessel, which is heated in an anthracene bath, and is provided with a double-walled copper lid also containing anthracene. The molten potash is raised to 250°, and at this temperature 150 gms. of dry finely powdered potassium sulphonate, as obtained above, is added all at once and well stirred in with a strong nickel spatula. The melt is then continued for two hours at 270° to 280° (inside temperature). The potassium dimethyl-*m*-aminophenolate which is formed separates as an oily layer on the surface. The melt is now cooled, dissolved in 3 litres of water, acidified with hydrochloric acid, and a little brown flocky precipitate filtered off. The filtrate is then neutralised with potassium bicarbonate, when dimethyl-*m*-aminophenol precipitates as an oil which soon solidifies. The separation can be completed by saturating the solution with salt. The liquid is now extracted with benzene, the benzene solution dried with potassium carbonate, and after distilling off the benzene, the residue is distilled under reduced pressure.

Another method of preparation of dimethyl-*m*-aminophenol is described on p. 101.

Diethyl-*m*-aminophenol—

$$N(C_2H_5)_2$$
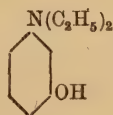
—melts at 78°, and boils at 276° to 280° (760 mm.) or 170° (15 mm.).

The method of G.P. 44792, quoted under dimethyl-*m*-aminophenol above, can be applied in this case also. An elaborate account of the manufacture by this method is given in Wolfrum's "Chemisches Praktikum," Part II., p. 326, from which it appears that the process used differs in two points from that described under the dimethyl compound. The sulphonation of diethylaniline is carried out at 125° instead of 60°, and caustic soda is used in place of caustic potash for the alkali fusion. The following is a brief summary of the process :

The diethylaniline (240 kg.) is run in a thin stream into 240 kg. of sulphuric acid, the temperature rising to about 75°. To the well-stirred sulphate so formed is added gradually 700 kg. of 40 per cent. oleum. The temperature rises to 125°, and is kept at this point for four hours. It is then cooled to 70°, and run into milk of lime made

from 800 kg. of slaked lime and about 6,000 litres of water. The lime having been exactly neutralised, a solution of 120 kg. of anhydrous sodium carbonate is added so as to form the sodium salt of the diethylanilinesulphonic acid. The solution is filtered and the filtrate concentrated somewhat. The caustic soda (350 kg.) required for the alkali fusion is now added and the solution evaporated until it reaches a temperature of 160° to 170°. This gives a mixture sufficiently dry to avoid overmuch foaming in the subsequent melt.

The fusion is carried out in lots of 25 kg. in special cast-iron tubes heated slowly in an oven to a temperature of 300°. The finished melts are dissolved in narrow tall vessels, acidified with sulphuric acid, and boiled to drive off sulphur dioxide. Sodium carbonate solution is then added until the solution is only faintly acid. The amino-phenol sulphate separates as an oily layer above the concentrated sodium sulphate solution. The latter is run off and the oil treated with dry sodium carbonate till a sample of the mixture on dilution with water shows no separation of oil. The oil so treated is then stirred with water and diluted, when the aminophenol separates as a flocky precipitate, which is filtered off. More aminophenol can be obtained from the filtrate, and from the previously separated sodium sulphate solution after allowing the sulphate to crystallise out, by extracting these solutions with ether. The crude product is purified by melting it in lots of 250 kg. and stirring into each 50 kg. of toluene, then allowing to crystallise. The yield is not quite definitely stated, but seems to be about 200 kg. of crude product (from 240 kg. of diethylaniline) or about 112 kg. of crystallised product.

Diethyl-*m*-aminophenol may also be prepared from resorcinol by a method similar to that described for dimethyl-*m*-aminophenol (p. 101).

Monoethyl-*m*-aminophenol—
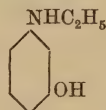
—m.p. 62°, b.p. 176° at 12 mm.

The preparation of this derivative is described in G.P. 48151 (Badische), the method used being essentially the same as that described for dimethyl-*m*-aminophenol (p. 22).

Another method of preparation, from *m*-phenylenediamineoxamic acid is given on p. 22.

Applications of the Alkyl-*m*-aminophenols.

These intermediates are used in the preparation of dyes of the Xanthene series by condensing them with various substances containing a reactive —CO— group in the molecule, such as phthalic anhydride, succinic anhydride, formaldehyde, and aromatic aldehydes, etc. Two molecules of the aminophenol take part in the condensation, which occurs in the *p*-position to each amino group, and is followed by ring closure with elimination of water :
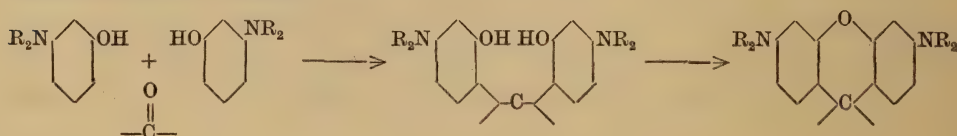
Using phthalic anhydride the Rhodamines are obtained. Only monoethyl- and diethyl-*m*-aminophenols give commercially usable dyes, the product obtained with the dimethyl compound being too sparingly soluble. It gives, however, a useful dye by condensation with succinic anhydride.

Unsymmetrical dyes are also made, since it is possible to condense phthalic anhydride with one molecular proportion of an alkylaminophenol, and then to condense the product with another alkylaminophenol or a resorcinol derivative.

Sulphanilic acid :

$$NH_2$$

$$SO_3H$$

The acid crystallises in two hydrated forms—(1) leaflets, with $2H_2O$; (2) needles, with $1H_2O$. The dihydrate, which is obtained by crystallisation from solutions below 19°, is very efflorescent, losing all its water of crystallisation on standing in the air. The monohydrate is much more stable and even in the desiccator only loses water slowly.

The following table gives the solubility of the acid in water :

Temperature (Degrees).	Gms. Anhydrous Acid per 100 Gms. Solution.	Corresponding Solid Phase.
0	0·44	Dihydrate.
7·2	0·62	,,
13·3	0·84	,,
18·9	1·09	,,
18·9	1·14	Monohydrate.
25·1	1·38	,,
31·1	1·66	,,
37·2	2·00	,,
44·0	2·44	,,
44·0	2·36	Anhydrous.
47·5	2·52	,,
54·5	2·85	,,

The sodium salt crystallises in leaflets with $2H_2O$.

While sulphanilic acid can be obtained by sulphonation of aniline with concentrated sulphuric acid (such a process is described by Groggins, "Aniline and its Derivatives," p. 160), it is usually made by the bake process from aniline sulphate. The former method requires a large excess of sulphuric acid and gives a product contaminated with isomers and disulphonic acid. The bake process requires only the theoretical amount of sulphuric acid and yields the *p*-sulphonic acid only. There is some indication that a sulphamic acid is formed as an intermediate stage :

$$NH_2.H_2SO_4 \xrightarrow{-H_2O} NH.SO_3H \longrightarrow NH_2, SO_3H$$
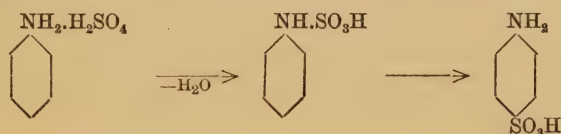
It has been found that the best results are obtained by using the exact amount of sulphuric acid required to form the sulphate of the base. An excess of either acid or base causes much oxidation, giving deeply coloured products, which are only with difficulty and much loss removed from the sulphanilic acid. The strength of the sulphuric acid used should, therefore, be accurately known. Another source of trouble is the presence of iron sulphate in the sulphuric acid. Traces of iron salts promote oxidation in the bake to a remarkable extent. Oxidation cannot be entirely avoided, but may be much diminished by attention to these points and by carrying out the reaction at the minimum temperature, which, in the case of aniline, is about 190°.

104 parts of the ordinary 95 per cent. sulphuric acid (or an equivalent quantity of acid of different strength) is added to 93 parts of aniline well stirred in a suitable vessel, which should not be of iron. A thick pasty mass of aniline sulphate is formed, and this is stirred till it is homogeneous. It is then spread thinly on trays (not of iron, but lead is suitable) and placed in an oven which is heated to 190°. For maintaining an even temperature, heating of the oven with superheated steam or circulating oil is best. A vacuum oven is also advantageous, as the necessary removal of water is thus accomplished more easily. Heating is continued till a test portion dissolves clear in soda solution. This requires about eight hours at 190°. The time required may be reduced to four to six hours by heating at 200° to 210°, but this is not advisable. The product is grey in colour and contains a little unchanged aniline. The yield is about 175 parts.

For purification it is dissolved in 500 parts of water containing 60 parts of soda ash, and the aniline distilled off with steam. The solution is then filtered, acid added till Congo paper is rendered blue, and on cooling the sulphanilic acid crystallises. It should be well cooled and allowed to stand for a considerable time before filtering off the crystals.

Sulphanilic acid is used as a first component in a large variety of monoazo, disazo, and trisazo dyes.

Phenylhydrazine-p-sulphonic acid :

$$\text{NH.NH}_2$$

$$\text{SO}_3\text{H}$$
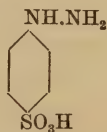
The acid forms lustrous colourless needles with $\frac{1}{2}\text{H}_2\text{O}$. It is sparingly soluble in cold water, but much more so in hot water.

The usual laboratory method of preparing aromatic hydrazines is to reduce the corresponding diazonium salt with stannous chloride and hydrochloric acid. For manufacturing purposes, however, it has been found preferable to use Fischer's original method (*Ann.*, 1878, **190,** 69) of reducing with sulphite. In the present case sulphanilic acid is diazotised and the diazonium salt treated with sodium sulphite. The first reaction which takes place is not a reduction, but the formation of a diazo-sulphonate :

$$SO_3H.C_6H_4.NH_2 \ + \ HNO_2 \ \longrightarrow \ SO_3.C_6H_4.N \vdots N$$

$$SO_3.C_6H_4.N \vdots N \ + \ Na_2SO_3 \ \longrightarrow \ SO_3Na.C_6H_4.N=N.SO_3Na$$
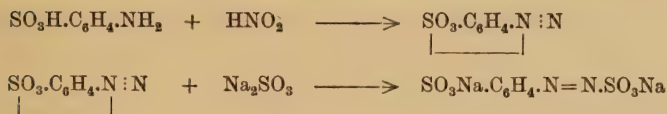
The diazosulphonate is then reduced to the hydrazinesulphonate :

$$SO_3Na.C_6H_4.N=N.SO_3Na \ + \ 2H \ \longrightarrow \ SO_3Na.C_6H_4.NH.NH.SO_3Na$$
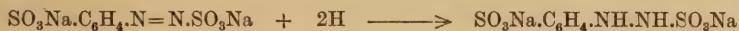
This reduction has sometimes been carried out by addition of zinc dust and acetic acid to the solution of diazosulphonate. But this is unnecessary, and is also comparatively costly. A simpler and quite effective method of reduction consists in adding a sufficient excess of sulphite beyond that required to form the diazosulphonate and then adding mineral acid. The nascent sulphur dioxide set free accomplishes the necessary reduction. Finally, the mineral acid, at a suitable temperature, hydrolyses the hydrazinesulphonate, the N-sulphonic acid group being split off as bisulphate :

$$SO_3Na.C_6H_4.NH.NH.SO_3Na \ + \ H.OH \ \longrightarrow \ SO_3Na.C_6H_4.NH.NH_2 \ + \ NaHSO_4$$

The preparation is carried out as follows :

173 gms. of sulphanilic acid is dissolved in 700 c.c. of water with addition of 56 gms. of soda ash. 115 gms. of concentrated sulphuric acid is then run in with stirring and the mixture cooled to 12°. The precipitated sulphanilic acid is diazotised at this temperature by slowly adding a solution of 70 gms. of sodium nitrite in 180 c.c. of water. A slight excess of nitrous acid should be shown by starch-iodide paper. The diazosulphanilic acid is even less soluble in water than sulphanilic acid. It is filtered off and washed with a little ice water.

Meanwhile 690 gms. of the ordinary 38 to 40 per cent. sodium bisulphite solution is carefully neutralised by addition of 35 per cent. caustic soda, using phenolphthaleïn as indicator. This is the most convenient method of making the required solution of neutral sodium sulphite. The addition of the alkali is continued until the indicator shows pink, when, by addition of a drop or two of bisulphite solution, the slight alkalinity is removed. It is important that the sulphite solution should not be alkaline, or tarry products are produced later.

The sulphite solution is stirred well, cooled to about 5°, and the diazosulphanilic acid (which should not have been allowed to dry, as the dry substance is explosive) is added, the temperature during mixing being kept about 5°. A yellow solution of diazosulphonate is formed, and this reaction is completed by allowing the solution to stand for an hour. The solution is then heated to boiling and concentrated hydrochloric acid added slowly until a strong mineral acid reaction shows on Congo Red paper. About 800 to 850 gms. of acid are required. Some sulphur dioxide is evolved, but most of it is, of course, used up in the reduction of the diazosulphonate to hydrazosulphonate. The completion of this reaction is shown by the solution becoming colourless. On cooling, phenylhydrazine-p-sulphonic acid crystallises out and, after standing for some hours, is filtered off and washed with a little water. The yield is about 165 gms.

Phenylhydrazinesulphonic acid is used in making pyrazolone derivatives.

Diphenylamine—
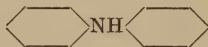
—crystallises in leaflets, m.p. 54°, b.p. 301·9° (760 mm.), 179° (22 mm.). D 1·16. It is insoluble in water, but soluble in methyl and ethyl alcohol and in ligroin.

The ordinary method of preparation of diphenylamine is to heat aniline with aniline hydrochloride at a high temperature, generally in an enamelled autoclave. There is much variation in the conditions used by different workers on this substance. As originally described by de Laire, Girard, and Chapoteaut (1866) (see Beilstein, II., 337), one molecule of aniline hydrochloride and $1\frac{1}{2}$ molecules of aniline are heated at 210° to 240° for thirty to thirty-five hours. A later description by Girard and de Laire ("Traité des dérivés de la houille," 1873, p. 418) gives 260° as the maximum temperature, and the proportion of aniline is reduced to 1 molecule. Fierz-David describes essentially the same process as the former one, heating for twenty hours at 230° and using 1·4 molecules of aniline to 1 molecule of aniline hydrochloride. He also states that the use of an enamelled autoclave (completely enamelled inside) is essential, since traces of iron or copper diminish the yield by 30 to 50 per cent., with formation of resinous products. Nevertheless, Flürscheim (U.S.P., 1212928) proposes to dispense with an enamelled autoclave by adding 430 parts of hydrated ferric chloride and 44·5 parts of copper powder to 892 parts of aniline, and heating to 238° to 240° in an ordinary iron autoclave. Finally, a so-called catalytic process is described in detail by Groggins ("Aniline and its Derivatives," p. 164), in which 2,000 lbs. of aniline mixed with 30 lbs. of concentrated hydrochloric acid is heated in a steel autoclave at 290° for forty hours.

In every case, the conversion of aniline to diphenylamine is incomplete. The autoclave contents, after the heating is finished, therefore consist chiefly of a mixture of diphenylamine and aniline. From this mixture the aniline is extracted by dilute hydrochloric acid. Diphenylamine can form a hydrochloride, but this is almost completely dissociated by water at even moderate dilution. The autoclave contents are, therefore, stirred up with about six times the weight of water at 80°, and hydrochloric acid added until the liquid shows acid to Congo Red paper. On cooling the undissolved layer of diphenylamine sets to a solid cake. This is filtered off and is washed again in succession with hot water, hot water containing a little hydrochloric acid, and finally with hot dilute soda solution, after which it is cooled, filtered off, and dried. The crude diphenylamine is purified either by fractional distillation in a vacuum or by distillation with superheated steam at 300°. In the latter case it is possible to distil 1 part of the base with 2 parts of steam. It collects as a colourless liquid, which sets to a pale yellow solid. Allowing for the aniline recovered from the wash liquors, which is usually about 30 to 35 per cent. of the aniline started with, the yield of diphenylamine is about 85 to 90 per cent. of the theoretical.

An essentially different method of preparation has been devised by Contardi (*Giorn. Chim. Appl.*, 1920, **1**, 11), based on the use of zinc chloride as condensing agent. It had been shown in some experiments by Merz and Weith that the double

compound of aniline and zinc chloride, $ZnCl_2.2C_6H_5.NH_2$, when heated in open vessels, even at high temperatures, yielded only traces of diphenylamine. Contardi, however, found that the double salt, $ZnCl_2.2(C_6H_5.NH_2.HCl)$, when heated with two molecular proportions of aniline, formed diphenylamine with evolution of ammonia, the reaction proceeding according to the equations :

1. $ZnCl_2.2(C_6H_5NH_2.HCl) + 2C_6H_5NH_2 = (C_6H_5)_2NH + NH_4Cl + ZnCl_2.2C_6H_5NH_2$

2. $ZnCl_2.2C_6H_5NH_2 + 2NH_4Cl = ZnCl_2.2(C_6H_5NH_2.HCl) + 2NH_3$

As the equations indicate, the preliminary preparation of aniline hydrochloride and its double salt with zinc chloride is unnecessary, all that is required being the addition of zinc chloride and ammonium chloride to the heated aniline. The zinc chloride, in fact, acts catalytically, but it seems to have been found necessary to use substantial quantities of it, at any rate, to start the reaction. However, after the addition of a small proportion of the required zinc chloride, the remainder may be substituted by a mixture of zinc oxide and ammonium chloride in the proportions necessary to form zinc chloride.

The actual method is as follows. 9 parts of aniline are heated to boiling in a vessel (which may be of wrought or cast iron) fitted with a reflux condenser and a stirrer, and 2·25 parts of recently fused zinc chloride, together with 1 part of ammonium chloride, are added gradually. (If zinc oxide and ammonium chloride are used to replace part of the zinc chloride, arrangement must be made, by keeping the condenser suitably warm, for the water formed to escape.) When the evolution of ammonia has ceased, the contents of the vessel consist of a mixture in about equimolecular proportions of diphenylamine and the double salt $ZnCl_2.2(C_6H_5NH_2.HCl)$. But, without further addition of zinc chloride, the formation of diphenylamine is continued by slow addition of aniline to the boiling liquid. Aniline may be added up to the capacity of the vessel used. This point having been reached and the ammonia having ceased coming off, the product is fractionally distilled. The first fraction consists of unchanged aniline, which may be used again. This is followed by almost pure diphenylamine. Yields up to 90 per cent. have been obtained.

The residue after distillation is chiefly the double chloride, together with a little diphenylamine and tarry matter. It was found that the process could then be repeated by simply adding aniline again to the boiling residue, and so on, five times in all before the apparatus required cleaning out.

Diphenylamine is chiefly used as a second component in monoazo dyes. As it is insoluble in water and its salts with mineral acids are dissociated by water, the coupling with diazo compounds is carried out in alcoholic solution.

Methyldiphenylamine—

$$\langle\quad\rangle N(CH_3)\langle\quad\rangle$$

—an oil, b.p. 291·7° to 292·2° (740·8 mm.). D_4^{20} 1·0476.

The methylation of diphenylamine by the usual method has been described by Girard (*Bull. Soc. Chim.*, 1875, **23**, 2). 100 kg. of diphenylamine, 68 kg. of con-

centrated hydrochloric acid, and 24 kg. of methyl alcohol were heated for ten to twelve hours in an enamelled autoclave at 200° to 250°. Methylation was not complete under these conditions. After setting free the bases by addition of alkali, they were separated and distilled. The distillate was shaken with two volumes of concentrated hydrochloric acid, which formed the hydrochlorides of both bases. Diphenylamine hydrochloride solidified and was filtered from the hydrochloride of the methyl compound, which remained liquid. The methylated base could then be isolated and purified in the usual way.

Methylation with dimethyl sulphate was used by Ullmann (*Ann.*, **327**, 113). 10 gms. of diphenylamine was warmed on the water-bath with 9·4 c.c. (1·2 mol₃.) of dimethyl sulphate. When the reaction was over, the product was made alkaline with caustic soda and distilled with steam. The yield of methyldiphenylamine was 8·5 gms. or about 80 per cent. It boiled sharply at 291°.

As a tertiary amine, methyldiphenylamine is used in making a few acid triphenyl-methane dyes of blue shades by condensing it with Michler's ketone or *p*-dimethyl-aminobenzoyl chloride and sulphonating the products.

Aminoazobenzene—

$$\langle\ \rangle\text{—N}=\text{N—}\langle\ \rangle\text{NH}_2$$
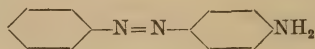
—crystallises in brownish-yellow needles, m.p. 127°. The hydrochloride forms dark steel-blue crystals.

Aminoazobenzene is prepared by intramolecular transformation of diazoamino-benzene under the catalytic influence of aniline hydrochloride. Diazoaminobenzene is formed by the action of diazotised aniline on aniline. The preparation, therefore, proceeds as follows :

1. $C_6H_5.NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5.N=N.Cl + NaCl + 2H_2O$

2. $C_6H_5.N=N.Cl + H_2N.C_6H_5 \longrightarrow C_6H_5.N=N.NH.C_6H_5 + HCl$

3. $C_6H_5.N=N.NH.C_6H_5 \xrightarrow[\substack{\text{In presence of} \\ C_6H_5.NH_2.HCl}]{} C_6H_5.N=N.C_6H_4.NH_2$
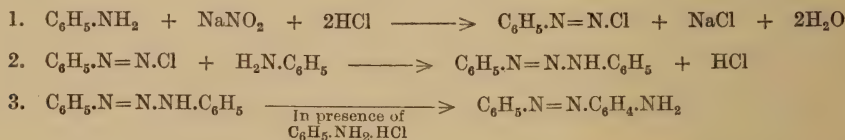
It is not necessary to prepare separately and to isolate the diazoaminobenzene. All that is required is to add nitrite to a sufficient excess of aniline and hydrochloric acid, and to warm the mixture of diazoaminobenzene, aniline hydrochloride, and aniline so formed at such a temperature that the transformation will take place. What constitutes a sufficient excess of aniline and hydrochloric acid ? As regards the acid, it will be noted from equations (1) and (2) that the net consumption of acid in the formation of diazoaminobenzene is 1 molecule per molecule of nitrite. Therefore, a little more than 1 molecule of acid must be used per molecule of nitrite in order that the excess may form the aniline hydrochloride required for the transformation. As regards the aniline, 2 molecules are required per molecule of nitrite for diazoamino-benzene. A slight excess over 2 molecules of aniline will then give the necessary aniline hydrochloride. But it is advisable to use a much larger excess of aniline than this, so that the free aniline may act as solvent for the diazoaminobenzene and aniline

hydrochloride, and thus enable the transformation to proceed more quickly and smoothly.

Processes, based essentially on the principles just outlined, are described by Paul (*Zeit. angew. Ch.*, 1896, **9,** 689), Jansen (*Zeit. Farb. Ind.*, 1913, **12,** 197), Fierz-David ("Farbenchemie," 1920, p. 190), and Groggins ("Aniline and its Derivatives," 1924, p. 200). The following table, in which are shown the relative quantities of materials used by the different authorities, is of interest as displaying the extent to which personal idiosyncrasy enters into the settling of the details of a chemical process.

Process.	Molecular Proportions of—			Yield of Aminoazobenzene (Molecules).
	$NaNO_2$.	HCl.	$C_6H_5.NH_2$.	
Paul	1	3·0	2·5	0·66
Jansen	1	1·05	7·7	—
Fierz-David	1	1·9	4·1	0·81
Groggins	1	1·1	11·0	—

The actual process, as described by Fierz-David (*loc. cit.*), is as follows. To 250 gms. of aniline 110 c.c. of concentrated hydrochloric acid is added with good stirring. The mixture is cooled externally to 32°, and at this temperature a solution of 45 gms. of sodium nitrite (100 per cent.) in a little water is added during half an hour. The temperature during the addition is not allowed to rise above 34°. After two hours, the temperature is raised to 40°, and after another hour at this temperature it is raised to 46° and kept there for three hours more. (The end of the transformation may be tested by dissolving a sample in glacial acetic acid and spotting a drop of this solution on filter-paper with an acetic acid solution of α-naphthylamine. If diazoaminobenzene is still present, a violet-red colouration is obtained by coupling of diazobenzene acetate with α-naphthylamine). The mixture is then added to 250 c.c. of water and 250 gms. of ice and concentrated hydrochloric acid stirred in till the liquid is definitely acid to Congo Red paper. The excess aniline is thus dissolved out, while the sparingly soluble aminoazobenzene hydrochloride remains undissolved. About 200 c.c. of hydrochloric acid are required. The aminoazobenzene hydrochloride is now filtered off and washed well with 10 per cent. salt solution containing also 2 per cent. of hydrochloric acid. A final wash with 2 per cent. hydrochloric acid is given to remove salt. The product is dried at 50°. This temperature must not be exceeded because of the danger of forming dyes of the Induline class.

Aminoazobenzene is used as a first component in azo dyes, its diazo compound being coupled mostly with naphthols and their sulphonic acids, thus forming disazo dyes, which are generally of bright red or scarlet shades.

It is also heated with aniline hydrochloride under various conditions to form mixtures of complex azine dyes known as the Indulines.

Aminoazobenzenesulphonic Acids.

Two sulphonic acids, a mono- and a disulphonic acid, are made and used as first components in the preparation of disazo compounds, chiefly of the Biebrich Scarlet type, by coupling with the naphthols and their sulphonic acids.

(*a*) **Monosulphonic acid :**

$$SO_3H \langle \quad \rangle N=N \langle \quad \rangle NH_2$$
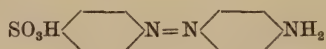
The acid crystallises in yellowish needles with $1\frac{1}{2}H_2O$, which are very sparingly soluble in water. 100 parts of water at 22° dissolve 0·0144 part of the acid. The calcium salt is also sparingly soluble, but the sodium salt is moderately soluble in water.

The preparation of this acid in pure condition and good yield offers some difficulty. The obvious method of coupling diazotised sulphanilic acid with aniline does not work. Coupling in the desired way takes place only to the extent of 15 to 20 per cent., some diazoamino compound being formed, and the rest remaining uncoupled. If, however, some easily hydrolysed derivative of aniline is used, the formation of diazoamino compound is prevented and yet coupling may proceed in the normal way in certain cases. In G.P. 217935 (A.G.F.A.) the aniline is acylated with *p*-toluenesulphon-chloride. The preparation then proceeds as follows. 173 parts of sulphanilic acid are dissolved in water and the necessary caustic soda, and diazotised as usual with nitrite and hydrochloric acid. The diazo compound is then added to a cooled solution of 247 parts of *p*-toluenesulphonanilide in about 1,800 parts of water and 160 parts of caustic soda solution (40° Bé). The *p*-toluenesulpho derivative of aminoazobenzene-sulphonic acid separates, and when coupling is finished is filtered off, washed, and dried. It is then stirred with 1,000 parts of concentrated sulphuric acid, and the mixture warmed at 40° until all has gone into solution, which takes about two hours. The toluenesulpho group is thus hydrolysed off. On pouring the solution into ice-water, the free aminoazobenzenesulphonic acid precipitates and is filtered off and washed.

By sulphonating aminoazobenzene a product may be obtained, which consists mostly of the same monosulphonic acid, but contains also some of the disulphonic acid, and possibly isomeric monosulphonic acids. This product is good enough for certain colours, though it does not give the desired shade and properties which are obtainable with the pure 4-sulphonic acid.

The sulphonation is carried out by stirring aminoazobenzene hydrochloride with three times its weight of 25 per cent. oleum at 25° until a sample just dissolves clear in dilute soda. At this point sulphonation to the monosulphonic acid is complete, and on pouring the solution into ice-water the crude sulphonic acid is precipitated and may be filtered off.

(*b*) **Disulphonic acid :**

$$SO_3H \langle \quad \rangle N=N \langle \quad \rangle \overset{\textstyle SO_3H}{\underset{\textstyle NH_2}{}}$$
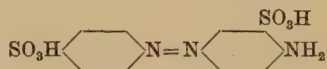
The acid forms violet-shimmering red needles which are somewhat soluble in water. The monosodium salt is flesh-coloured and is much less soluble than the acid, but the disodium salt, which is yellow, is very soluble in water.

The disulphonic acid is prepared by continuing the sulphonation process described above for the monosulphonic acid. When monosulphonation is complete, the solution is raised to 40° and stirred well at this temperature until a sample is found to be completely soluble in a large proportion of water. The solution is then poured on to six times its weight of ice, and on adding salt till a 20 per cent. solution is obtained the monosodium salt is salted out. This is filtered off and washed with 15 per cent. salt solution.

The disodium salt is itself used as a dyestuff, under the name Acid Yellow or Fast Yellow, but the chief use of the disulphonic acid is for the production of scarlet disazo dyes by coupling its diazo compound with the naphthols and their sulphonic acids. Aminoazobenzenemonosulphonic acid is used in a similar way.

Phenylglycine :

$$\langle\ \rangle\text{NH.CH}_2.\text{COOH}$$

The acid forms white crystals, m.p. 127°, moderately soluble in water. The sodium and potassium salts are easily soluble, the calcium salt sparingly soluble, and the iron and copper salts insoluble in water.

The preparation of phenylglycine has been the subject of much investigation, due to its importance as an intermediate for Indigo. The methods followed are of three kinds :

1. The condensation of aniline with chloroacetic acid.

2. The formation of the nitrile of phenylglycine by means of formaldehyde and cyanides, followed by hydrolysis of the nitrile.

3. The condensation of aniline with trichloroethylene, followed by hydrolysis of the product.

Each of these methods will be dealt with in turn.

1. Condensation of Aniline with Chloroacetic Acid.

This reaction does not take the simple course indicated by the equation :

$$\text{C}_6\text{H}_5.\text{NH}_2\ +\ \text{Cl.CH}_2.\text{COOH}\ =\ \text{C}_6\text{H}_5.\text{NH.CH}_2.\text{COOH}\ +\ \text{HCl}.$$

If equimolecular quantities of aniline and chloroacetic acid are heated together at 100°, some phenylglycine is formed, but there is also much phenyliminodiacetic acid $\text{C}_6\text{H}_5.\text{N(CH}_2.\text{COOH)}_2$, some ω-chloroacetanilide, $\text{Cl.CH}_2\text{CO.NH.C}_6\text{H}_5$, some diphenyl-diketopiperazine—

$$\text{C}_6\text{H}_5.\text{N}\underset{\text{CO---CH}_2}{\overset{\text{CH}_2\text{---CO}}{\langle\qquad\rangle}}\text{N.C}_6\text{H}_5$$
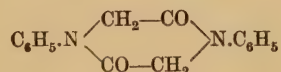
—and some unchanged aniline. The tendency towards formation of phenylimino-diacetic acid may be diminished by using an excess of aniline. Using 2 molecules of aniline per molecule of chloroacetic acid and heating the two in water, de Mouilpied (*J.C.S.*, 1905, **87**, 438) obtained a yield of 70 to 80 per cent. of phenylglycine, containing a small proportion of phenyliminodiacetic acid. The use of 3 molecules of aniline

per molecule of chloroacetic acid seems almost entirely to prevent the formation of the diacetic acid derivative.

But with the use of excess of aniline another by-product appears—namely, phenyl-glycineanilide, $C_6H_5.NH.CH_2.CO.NH.C_6H_5$—formed by condensation of the first formed phenylglycine with aniline. This, however, can be reconverted to phenyl-glycine by hydrolysis with alkali.

The isolation of phenylglycine from the reaction mixture may be carried out by addition of sufficient alkali (e.g., soda) to set free excess aniline from its hydrochloride, and distilling off the aniline with steam. This leaves an aqueous solution of the sodium salt of phenylglycine accompanied by sodium chloride. If this is acidified, phenylglycine is precipitated, but its solubility even in cold water is such that a substantial amount remains in solution and is lost. On the other hand, evaporation of the solution of the sodium salt to dryness would give a product containing sodium chloride which would cause trouble in the subsequent alkali fusion of the phenyl-glycine.

A process has been patented by the Badische Aniline Co. (G.P. 169358), in which these difficulties are overcome by converting the phenylglycine completely to the anilide, a very sparingly soluble substance which may be separated without loss and then hydrolysed by a molecular proportion of caustic soda, thus yielding a solution containing the sodium salt of phenylglycine only. Two methods of carrying this out are described. In the first, 500 kg. of aniline and 100 kg. of chloroacetic acid are heated first at 100° for three hours, then at 120° in a vacuum, until no more water is evolved. A solution of phenylglycineanilide and aniline hydrochloride in aniline is thus obtained. Sodium carbonate is added, and the free aniline is distilled off with steam. Under these conditions no hydrolysis of phenylglycineanilide takes place. On cooling the residual liquid, the anilide solidifies to a crystalline cake. This is separated and heated with one molecular proportion of caustic soda solution in an autoclave at 140° to hydrolyse the anilide. After steam-distilling off the aniline set free by hydrolysis, the remaining solution is evaporated to dryness in a vacuum. In the second method, the aniline and chloroacetic acid are refluxed with 200 litres of water for three hours. The water is then distilled off under reduced pressure and the distillation continued, while the temperature of the melt rises to 120° to 140°, until no more water comes over. The melt is now cooled, stirred with caustic soda solution, which extracts the hydrochloric acid formed during the reaction, and the mixture allowed to settle. The aniline layer containing phenylglycineanilide in solution is separated and is hydrolysed with aqueous caustic soda (1 mol. NaOH to 1 mol. phenylglycineanilide) in an autoclave at 140° as before. The aniline is then distilled off with steam and the remaining solution evaporated to dryness.

Another method of overcoming the difficulty of the formation of phenylimino-diacetic acid or phenylglycineanilide by further action on the first formed phenyl-glycine consists in the removal of the phenylglycine from the sphere of reaction, as it is formed, by conversion into an insoluble salt. For this purpose the ferrous salt seems to be particularly well suited. The large excess of aniline required in other methods may also be dispensed with. Meister Lucius and Brüning have patented a

process of this kind (G.P. 177491), in which the molecular ratio of aniline to chloro-acetic acid is reduced to 1·1 : 1. A solution of 1,250 kg. of ferrous chloride in water is precipitated by adding caustic soda or carbonate. 300 kg. of salt are added, and the mixture heated to 90° to 100°. At this temperature 472 kg. of chloroacetic acid is added, followed quickly by 510 kg. of aniline. Heating is now continued under reflux for one and a half hours. After cooling, the insoluble iron salt of phenylglycine is filtered off, washed with cold water, and then converted into the sodium salt by stirring with water and adding the required carbonate or caustic soda. Any aniline present is distilled off with steam, the mixture filtered from iron oxide or carbonate, and phenyl-glycine precipitated from the filtrate by careful addition of dilute acid.

Other processes are described by Chemische Fabrik von Heyden (E.P. 14049 of 1902), Friswell (E.P. 18149 of 1907), Chemische Fabrik Weiler-ter-Meer (G.P. 244825) and Wohl and Blank (G.P. 167698).

2. Intermediate Formation of the Nitrile.

According to G.P. 135332 (Meister Lucius and Brüning), aniline reacts with formaldehyde and a cyanide thus—

$$C_6H_5.NH_2 + CH_2O + NaCN + H_2O = C_6H_5.NH.CH_2.COONa + NH_3$$

—and a process of preparation of phenylglycine on these lines is described in the patent. But it was shown later by the Basle Chemical Works, in G.P. 145376, that the maximum yield obtainable by the above method was about 60 per cent., and that much better results could be obtained by previously condensing formaldehyde with two molecular proportions of aniline so as to form methylenedianiline, $C_6H_5.NH.CH_2.NH.C_6H_5$, which then reacted with cyanide as follows :

(a) $C_6H_5.NH.CH_2.NH.C_6H_5 + KCN + H_2O = C_6H_5NH.CH_2.CN + KOH + C_6H_5.NH_2.$

(b) $C_6H_5.CH_2.CN + KOH + H_2O = C_6H_5.NH.CH_2.COOK + NH_3$
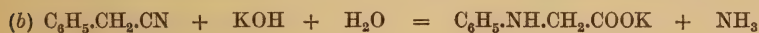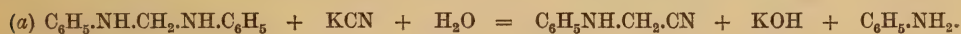
Probably the low yield in the earlier process is due to the reaction taking this course to a large extent. The Basle Chemical Works, therefore, proceed as follows. A mixture of 186 kg. of aniline (2·1 mols.), 200 litres of alcohol, and 5 litres of 30 per cent. caustic potash or soda is treated with 80 kg. of 37·9 per cent. formalin and the solution heated to boiling. At the boil, 132 litres of a 49·3 per cent. solution of potassium cyanide, previously warmed, is run in. A fairly vigorous reaction takes place with evolution of ammonia, and after half an hour's heating complete solution is obtained. The alcohol and aniline are now distilled off and the residual solution of potassium salt of phenylglycine evaporated to dryness. Yields of over 90 per cent. are obtained.

The nitrile may also be formed by interaction of a cyanide with the methyl-ω-sulphonate of aniline, a method introduced by Bucherer, who describes the process as follows (G.P. 157909) : A mixture of 75 gms. of 40 per cent. formalin and 260 gms. of 40 per cent. bisulphite is warmed for a short time on the water-bath until the smell of formaldehyde has disappeared. A solution of " formaldehyde-bisulphite,"

OH.CH$_2$.SO$_3$Na, is thus formed.   To this is added 93 gms. of aniline and the mixture stirred at 90°.   Soon the aniline disappears with formation of sodium methylaniline-ω-sulphonate, C$_6$H$_5$.NH.CH$_2$.SO$_3$Na.   A solution of 70 gms. of 95 per cent. potassium cyanide (or equivalent sodium cyanide) in 200 c.c. of water is now added, and in a short time the nitrile has separated completely.   The whole process requires only a fraction of an hour :

$$C_6H_5.NH.CH_2.SO_3Na \; + \; NaCN \; = \; C_6H_5.NH.CH_2.CN \; + \; Na_2SO_3$$
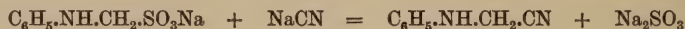
The conversion of the nitrile to phenylglycine is not described in the patent.   Presumably it would be best to filter off the nitrile, thus getting rid of the sulphite, before hydrolysing with an equivalent of alkali.

3. Condensation of Aniline with Trichloroethylene.

The fact that trichloroethylene is easily converted into chloroacetic acid naturally suggests the possibility of preparing phenylglycine by condensing trichloroethylene with aniline and hydrolysing the product.   Dichlorovinyl ether, C$_2$HCl$_2$.OC$_2$H$_5$, which is a product of partial hydrolysis of trichloroethylene, had been condensed with aniline under hydrolytic conditions so as to yield phenylglycine ester, by Imbert (E.P. 13176 of 1907; E.P. 5013 and 5014 of 1907).   But he succeeded later in carrying out the condensation with trichloroethylene itself.   Apparently the reaction proceeds through the intermediate formation of ethylenetriphenyltriamine by elimination of hydrochloric acid from 1 molecule of trichloroethylene and 3 molecules of aniline.   This base had previously been made by Sabanejeff (*Ann.*, **178**, 125).   The next stage of the reaction is the hydrolysis of Sabanejeff's base to phenylglycineanilide, followed by a final hydrolysis to phenylglycine.

$$\begin{array}{c}CHCl \\ \parallel \\ CCl_2\end{array} \; + \; 3C_6H_5.NH_2 \; \xrightarrow[-3HCl]{} \; \begin{array}{c}HC-NH.C_6H_5 \\ \mid \\ N.C_6H_5 \\ \mid \\ HC-NH.C_6H_5\end{array} \; \xrightarrow[+H_2O]{} \; C_6H_5.NH.CH_2.CO.NH.C_6H_5$$

$$\xrightarrow{\hspace{2cm}} \; C_6H_5.NH.CH_2.COOH$$
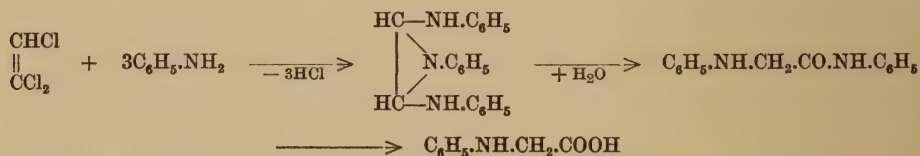
There is no necessity, of course, to isolate the intermediate bodies.   The process is described in E.P. 173540 (B.D.C., Levinstein and Imbert).

132 parts of trichloroethylene, 100 parts of lime, 800 parts of water, and 280 parts of aniline are heated together in an autoclave with good stirring for twenty-four hours at 180°.   After cooling, the excess of aniline is distilled off.   The residual liquor contains the calcium salt of phenylglycine and excess lime in suspension, and calcium chloride, together with a little phenylglycine calcium salt in solution.   When cold the mixture is filtered.   (The small amount of phenylglycine calcium salt in the filtrate may be precipitated as ferrous salt.)   The solid residue is now boiled with the necessary quantity of sodium carbonate or hydroxide to convert the calcium salt to sodium salt. This is filtered free of lime, and the filtrate evaporated to dryness.

It will be noticed that the proportion of 3 molecules of aniline to one of trichloro-

ethylene is used in the above process, in accordance with the theory of the reaction previously given.   And, in fact, if less aniline is used the yield of phenylglycine is much diminished when the process is carried out as above.   But an improved process has been devised (E.P. 188933, Wyler and B.D.C.), in which the excess of aniline is cut down to about 5 per cent.   This is achieved by adding the trichloroethylene gradually to the mixture of aniline and milk of lime, so that from start to finish the trichloroethylene present always finds three molecular proportions of aniline to react with.

412 parts of aniline, and milk of lime, made from 504 parts of lime and 2,000 parts of water, are heated with stirring in an autoclave to 170° and, during ten hours, 555 parts of trichloroethylene are pumped in, the temperature being maintained at 170° to 180.°   The small amount of unchanged aniline is distilled off and the residual calcium salt worked up as described in the previous patent.

Quinoline—

—a colourless, strongly refracting liquid of characteristic smell.   It freezes at − 19·5°, and boils under various pressures as follows : 238° (760 mm.), 132° (40 mm.), 118·2° (20 mm.), 113·3° (16 mm.), 104·8° (9 mm.).   Its specific gravity compared with water at 4° is 0·9211 (234°), 1·069 (50°), 1·0947 (20°), 1·1081 (0°).   It is moderately soluble in water, 100 parts of cold water dissolving about 6 parts of quinoline.   It is very hygroscopic and absorbs, on standing in moist air, at 10°, water corresponding to 1·5 H_2O. On warming this hydrate to 40° it dissociates and becomes cloudy in appearance.

Quinoline is a strong base and forms a crystalline hydrochloride, m.p. 93° to 94°, soluble in chloroform and alcohol in all proportions and also in warm ether and benzene.

The method of preparation was discovered by Skraup (*Mon.*, 1881, **2,** 141), who heated aniline with glycerine, sulphuric acid, and nitrobenzene, the last serving as an oxidising agent.   The glycerine is converted by the sulphuric acid to acroleïn, $CH_2 : CH.CHO$, which Skraup supposed to condense with aniline to give the Schiff base, $C_6H_5.N : CH.CH : CH_2$, this being then oxidised to quinoline :
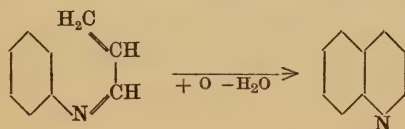
Later investigation showed that the reaction more probably takes the course :
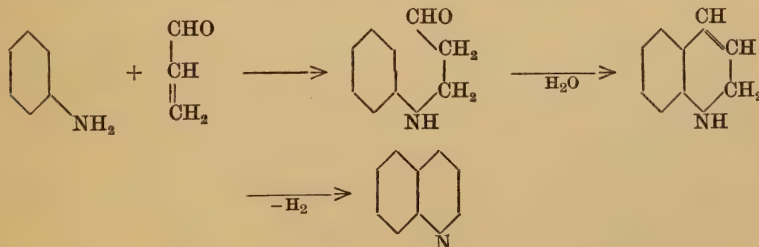
However, the fact that there is always a considerable quantity of aniline left after the reaction is over indicates that both the Schiff base and the addition product are formed, and that while the latter is converted into quinoline, the former is unaffected until the reaction mixture is diluted with water, when it is simply hydrolysed, like other Schiff bases, to aniline and the aldehyde acroleïn again.

Other oxidising agents have been used in place of nitrobenzene, giving, it is claimed, better yields of quinoline. Skraup obtained 55 parts of quinoline from 50 parts of aniline and 32 parts of nitrobenzene, a yield of less than 50 per cent., and this yield has not been substantially improved upon by later workers with his method. But, using arsenic oxide, As_2O_5 (Knüppel, *Ber.*, 1896, **29**, 703; G.P. 87334), a yield of 67 per cent. is obtained. Calcined ferric oxide (Barnett, *Chem. News*, 1920, **121**, 205) as oxidant leads to a 60 per cent. yield of quinoline. Chloropicrin, $CCl_3.NO_2$, has also been proposed (E.P. 198462).

The following description is based on Knüppel's method. 50 parts of aniline, 155 parts of glycerin, 76 parts of arsenic oxide, and 145 parts of concentrated sulphuric acid are well mixed in a vessel provided with a wide-bore reflux condenser. The mixture is then heated cautiously until an appearance of boiling begins to show in the liquid, when external heating is stopped. The reaction proceeds very vigorously of itself, once started, and external cooling may even be required to moderate it. When this reaction is over, the liquid is boiled for about three hours. It is then diluted with water, made alkaline with caustic soda solution, and the quinoline and aniline distilled with steam. The total distillate is made strongly acid with sulphuric acid, cooled to 0° to 5°, and a saturated solution of sodium nitrite added until excess nitrous acid shows on starch-iodide paper. The aniline is thus diazotised, while the quinoline is unaffected. The solution is heated on the water-bath until evolution of nitrogen, due to conversion of benzenediazonium chloride into phenol, ceases. On making alkaline again with caustic soda and steam distilling, quinoline alone distils with the steam. Most of the quinoline may be separated directly from the distillate, but part is dissolved in the water and is extracted with ether or benzene. The extract is dried and the solvent distilled off. The crude quinoline is then distilled under reduced pressure. The fraction collected at 110° to 114° under 14 mm. pressure is fairly pure quinoline. The yield obtained is about 46 parts.

Quinoline is used in the preparation of photosensitising dyes (see the Colour Index, Nos. 805 to 809).

Quinaldine—
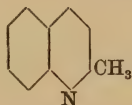
—a colourless oil, b.p. 246° to 247°, having a faint smell resembling that of quinoline.

This substance was first prepared by Döbner and von Miller (*Ber.* **16**, 2465) by warming a mixture of 1 part of aniline, 1½ parts of paraldehyde, and 2 parts of concentrated hydrochloric acid for a few hours on the water-bath. It was shown later that the reaction proceeded essentially according to the equation :

$$C_6H_5.NH_2 \ + \ 2CH_3.CHO \ = \ C_{10}H_9N \ + \ 2H_2O \ + \ H_2$$

No hydrogen is evolved, however. It is evidently used up in reducing part of the reaction mixture. The mechanism of the reaction seems to consist in the formation of crotonaldehyde, $CH_3.CH : CH.CHO$, by condensation of 2 molecules of acetaldehyde, followed by addition of the crotonaldehyde to aniline and finally ring closure to quinaldine in a manner similar to that explained under quinoline :
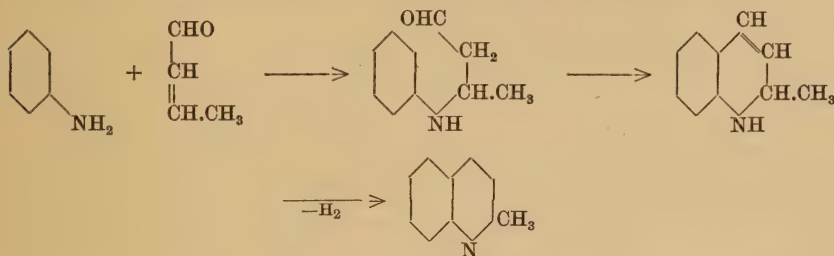
It was considered by Jones and Evans (*J.C.S.*, 1911, **99**, 334) that the hydrogen was used up in reducing part of the quinaldine to tetrahydroquinaldine—
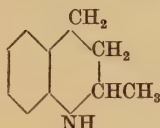
—which differs from quinaldine in being a secondary base and, therefore, capable of being benzoylated. Recently, however, Mills, Harris, and Lambourne (*J.C.S.*, 1921, **119**, 1294) have shown that, in fact, quinaldine prepared by the Döbner-Miller process is accompanied by little or no tetrahydroquinaldine, but that the secondary bases which are formed in considerable quantity contain *n*-butylaniline, a substance closely resembling tetrahydroquinoline in composition and character. This implies that the crotonaldehyde in part condenses with aniline to form the Schiff base, crotonylidene-aniline, which is reduced by the hydrogen eliminated in the main reaction to *n*-butylaniline :

$$C_6H_5.N : CH.CH : CH.CH_3 \ + \ 4H \ \longrightarrow \ C_6H_5.NH.CH_2.CH_2.CH_2.CH_3$$
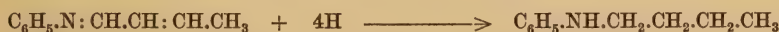
Some ethylaniline is formed in a similar way by reduction of ethylideneaniline produced from aniline and part of the acetaldehyde.

Mills, Harris, and Lambourne (*loc. cit.*) describe the preparation of quinaldine by a modified Döbner-Miller method, zinc chloride being added to the reaction mixture (as originally proposed in G.P. 24317). Acetaldehyde (350 gms.), in the form of the commercial 75 per cent. solution, is added slowly to a well-stirred mixture of 300 c.c. of aniline and 1,200 c.c. of concentrated hydrochloric acid, cooled in ice-water. After allowing the solution to stand for half an hour, 240 gms. of zinc chloride are added, and the solution heated gently under reflux until a vigorous reaction begins. When this has subsided, the liquid is boiled for four to six hours. It is then poured on excess of slaked lime and the mixture distilled with steam until 12 litres of distillate have

collected. The oil is then separated from the aqueous layer and the dissolved bases extracted from the latter by a little chloroform. The crude oil (500 c.c.) is dissolved in dilute sulphuric acid and a slight excess of nitrite added to the ice-cooled solution. The secondary bases are thus converted into nitrosamines, which separate as an oil. They are at once extracted with ether. The aqueous layer is then heated on the water-bath, made alkaline with caustic soda, and the tertiary bases distilled with steam. About 315 c.c. are obtained. On fractionation this distils almost entirely about the boiling-point of quinaldine. A small fraction, 3·5 gms., boils at a much higher temperature, 276° to 282°, and consists of 6-ethylquinaldine.

The following is given as the technical method of preparation by Ullmann : 30 kg. of aniline salt is stirred with 40 to 50 litres of water and 24 kg. of acetaldehyde run in during five to six hours, the temperature being maintained by cooling at 25°. The mixture is allowed to stand at 25° for two to three days, until a sample warmed with caustic soda solution no longer separates oil. (Instead, white flocks of a base, $C_{18}H_{20}N_2$, separate as described in G.P. 28217.) After adding 40 kg. of zinc chloride solution (50° Bé), the mass is evaporated to dusty dryness in a copper vessel. It is then melted and the temperature raised to 275° for a short time. It is then transferred to a still, 150 litres of water, and 50 kg. of caustic soda solution (40° Bé) added so as to give a strong alkaline reaction, and the quinaldine distilled in steam, while the contents of the still are continuously stirred. The crude quinaldine is separated from the distillate and is fractionated. The fraction distilling at 230° to 270° is taken as technically pure quinaldine. The yield is 17 kg. of quinaldine from 30 kg. of aniline.

Quinaldine is used in the preparation of photosensitising dyes (Colour Index, Nos. 805 to 809). It is also condensed with phthalic anhydride to form Quinoline Yellow.

α-Isatinanilide—
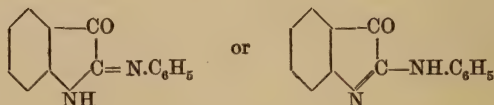
—crystallises from benzene in lustrous violet-black needles, m.p. 126°. From alcohol it crystallises in orange-red leaflets. It dissolves easily in hot alcohol, ether, benzene, and carbon disulphide. Its solution in alcohol is yellowish-brown, but in benzene or carbon disulphide is cherry-red. It also dissolves easily in mineral or organic acid solutions, forming salts. The mineral acid solutions on long standing, or more quickly on warming, decompose with formation of isatin and aniline.

α-Isatinanilide is prepared from aniline by the method discovered by Sandmeyer of which he gives an interesting account in the *Zeitschrift für Farben- und Textil-Chemie*, 1903, **2**, 129 (*cf.* also *Helv. Chim. Acta.*, 1919, **2**, 234). The method is also embodied in a series of patents by Geigy and Co. (G.PP. 115169, 113978, 113980, 113981).

It depends on the following set of reactions, starting from thiocarbanilide,

which apparently reacts in this case, as also in other cases, in its tautomeric form :

$$\text{Thiocarbanilide} \quad \xrightarrow[+ \text{PbCO}_3]{+ \text{NaCN}} \quad \text{Hydrocyancarbodiphenylimide}$$

$$\xrightarrow{+ \text{H}_2\text{S}} \quad \text{Thio-oxamidediphenylamidine (`` Thioamide '')} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \alpha\text{-Isatinanilide}$$
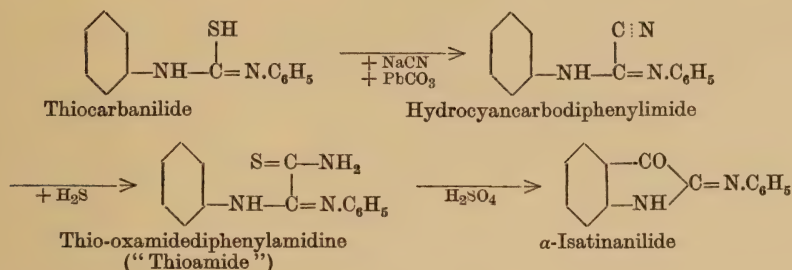
(i.) **Thiocarbanilide.**—This is prepared by boiling aniline with an equal weight of carbon disulphide under reflux until evolution of hydrogen sulphide ceases. The excess of carbon disulphide is then distilled off and the residue raised to a temperature a little above the melting-point of thiocarbanilide, when the liquid can be poured out and powdered when cold. The yield is quantitative.

The reaction, which takes about two days to complete under the above conditions, can be accelerated by the addition of alcohol and caustic potash.

Thiocarbanilide melts at 154°.

(ii.) **Hydrocyancarbodiphenylimide.**—A solution of 70 gms. of 96 to 98 per cent. potassium cyanide (or 53 gms. of sodium cyanide) in 200 gms. of water is mixed with 300 gms. of basic lead carbonate (white lead), 200 gms. of very finely powdered thio-carbanilide, and 500 gms. of 90 per cent. alcohol. The whole is stirred and slowly heated to 50° to 60°, at which temperature it is kept until the reaction is finished, as shown by a sample, filtered from lead sulphide, giving a filtrate which no longer blackens lead carbonate on boiling. When this point is reached, which only requires a short time, the mixture is heated to boiling, filtered hot, and the residue extracted twice with alcohol. On cooling the united filtrates most of the product crystallises out, and more can be obtained by concentrating the mother liquor. The yield is about 175 gms. and the substance is obtained as pale yellow prisms, m.p. 137°.

(iii.) **Thioamide.**—200 gms. of finely powdered hydrocyancarbodiphenylimide is stirred vigorously with 500 gms. of yellow ammonium sulphide solution. The latter is made by passing 35 gms. of hydrogen sulphide into 400 gms. of 21 to 22 per cent. ammonia and dissolving in the, as yet, colourless solution 25 gms. of powdered sulphur. The temperature of the mixture is kept about 25° to 35°, until a sample, filtered and well washed, dissolves completely in dilute hydrochloric acid. The rate of addition of the hydrogen sulphide depends on the fineness of division of the hydro-cyancarbodiphenylimide, and may take two days. The thioamide is then filtered off, washed, and dried. It forms a lemon-yellow powder, which is pure enough for the next stage. It may be purified by crystallisation from alcohol, when it is obtained as lustrous golden yellow prisms, m.p. 161° to 162°. It is soluble in dilute mineral acid and also, on warming, in dilute caustic soda.

(iv.) **α-Isatinanilide.**—The conversion of the thioamide to isatinanilide is accomplished by heating with sulphuric acid, but it is necessary to add the thioamide to the

previously heated acid. If the thioamide is added to cold acid and slowly heated, so much decomposition occurs that only a little isatinanilide results.

To 800 gms. of concentrated sulphuric acid at 90° is added with stirring 200 gms. of well-dried thioamide. Much heat is developed, and cooling arrangements must be made so as to keep the temperature from rising above 95°. These temperature limits are important. A vigorous evolution of sulphur dioxide takes place, and the thio-amide dissolves, giving at first a dark brown-violet solution, which finally becomes intense yellowish-red. When all the thioamide has been added, the temperature is raised to 105° to 110°, and kept there till evolution of sulphur dioxide ceases, which takes about an hour. The solution is then cooled to the ordinary temperature and run into a mixture of ice and salt solution. The isatinanilide is thus precipitated as its red crystalline hydrochloride, mixed with sulphur. It is filtered off, washed acid-free with concentrated salt solution, stirred into water, and dilute sodium carbonate solution added till faintly alkaline. The mixture of brown isatinanilide and sulphur is filtered off, washed, and dried. The sulphur is extracted with carbon disulphide, and the isatinanilide crystallised from benzene or alcohol. The yield is 150 gms. of recrystallised substance.

α-Isatinanilide is readily converted into Indigo by the action of hydrogen sulphide in acid solution, and Indigo was at one time made by this process. It was abandoned because of the lower cost of the phenylglycine fusion with sodamide. Isatinanilide, however, is most conveniently made by the above method, and is used as an intermediate for a number of vat dyes. These are prepared by condensing isatinanilide with various substances containing in the molecule the group —CO—CH₂— or its tautomeric form —C(OH)=CH—. Examples of such bodies are hydroxythio-naphthene (thioindoxyl, p. 208), α-naphthol (p. 145), α-anthrol (p.232). Thus, with thioindoxyl :
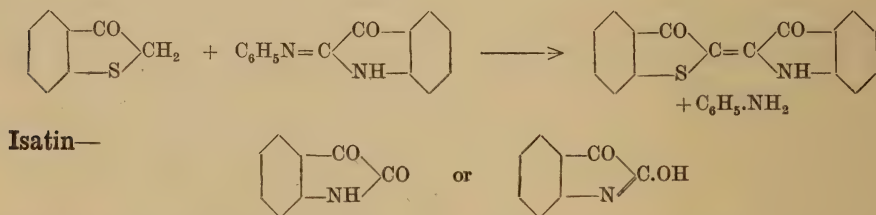
—crystallises in yellowish-red prisms, m.p. 200° to 201°, sparingly soluble in cold water, but easily in hot water and in boiling alcohol or benzene. It dissolves in cold dilute alkali to a dark violet solution, from which it is reprecipitated by acids. But if the alkaline solution is warmed, the colour changes to pale yellow owing to hydrolysis of the isatin to o-aminobenzoylformic acid :
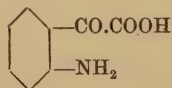
This can be reconverted to isatin by warming with acids.

Isatin was formerly prepared by oxidation of Indigo, but poor yields are obtained in this way.

It is readily prepared by heating α-isatinanilide with dilute mineral acid, preferably hydrochloric acid, when hydrolysis takes place and aniline is split off, the isatin being precipitated (G.P. 113979, Geigy) :

$$\begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!C=N.C_6H_5 \quad \xrightarrow{+\;H_2O} \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CO \;+\; C_6H_5.NH_2$$
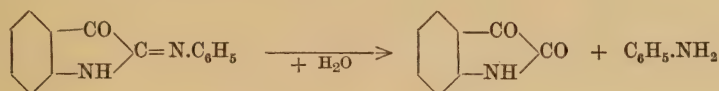
The isatin is filtered off and recrystallised from hot water.

Either of the usual processes for the manufacture of Indigo—*i.e.*, the phenylglycine and phenylglycine-*o*-carboxylic acid processes—can be adapted to the preparation of isatin by adding *strong* oxidising agents to the melt when the formation of indoxyl or indoxylic acid is complete. *Weak* oxidising agents, of course, convert the indoxyl or indoxylic acid into Indigo :

$$-NH.CH_2.COOH \quad \longrightarrow \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CH_2 \quad \xrightarrow{+2\,O} \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CO$$

<div align="center">Indoxyl</div>

$$\begin{array}{c}-COOH\\ \\-NH.CH_2.COOH\end{array} \quad \longrightarrow \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CH.COOH \quad \xrightarrow{+2\,O} \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CO$$
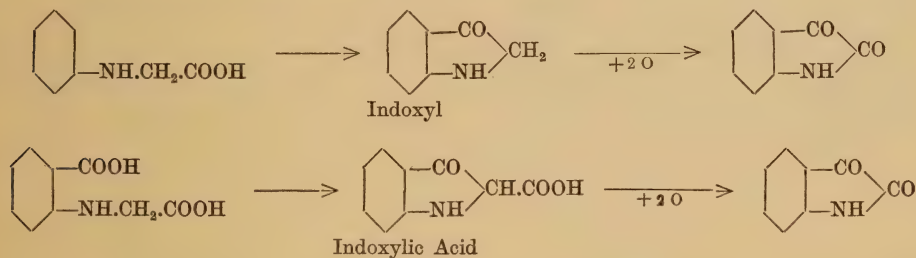
<div align="center">Indoxylic Acid</div>

Thus, according to G.P. 107719 (Badische), 7 parts of indoxylic acid are added to a solution at 80° of 6 parts of potassium permanganate and 10 parts of caustic soda in 50 parts of water. When the solution is decolourised, the manganese dioxide is filtered off, the filtrate exactly neutralised, evaporated to small bulk, and excess of mineral acid added, when on cooling the isatin crystallises out.

Alternatively, 8 parts of indoxyl in aqueous solution are added slowly to a boiling mixture of 20 parts of manganese dioxide (regenerated), 30 parts of water, and 7 parts of caustic soda solution (25° Bé). When the oxidation is completed, the isatin is isolated as above.

The yields of isatin in this process are said to be much better than those from Indigo itself.

Isatin is used for the preparation of vat dyes by condensation with indoxyl and thioindoxyl. Unlike α-isatinanilide, however, it is the β-carbonyl group in isatin which reacts :

$$\begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!CH_2 \;+\; OC\!\!<\!\!\begin{array}{c}OC-\\ \\HN-\end{array} \quad \longrightarrow \quad \begin{array}{c}-CO\\ \\-NH\end{array}\!\!\!\!\!>\!C\!\!=\!\!C\!\!<\!\!\begin{array}{c}-\\OC\\HN-\end{array}$$

<div align="center">Indirubin</div>

Thioindigo Scarlet
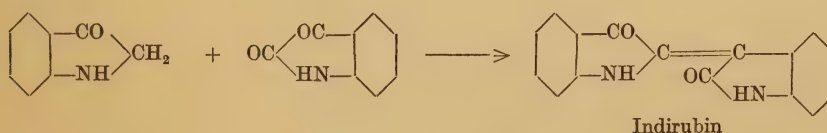
Indirubin itself is not used as a dyestuff, but a brominated derivative constitutes Ciba Heliotrope.

α-**Isatin chloride**—
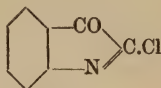
—crystallises in brown needles, m.p. 180°, soluble in alcohol, glacial acetic acid, and hot benzene. It also dissolves in ether to a blue solution.

The preparation of this substance is described by Baeyer (*Ber.*, **12,** 456). 5 parts of isatin are warmed on the water-bath with 6 to 7 parts of phosphorus pentachloride and 8 to 10 parts of dry benzene. On cooling the isatin chloride crystallises and is filtered off and washed with ligroin.

α-Isatin chloride, like α-isatinanilide, reacts in the α-position with indoxyl and thioindoxyl or their derivatives, and is used for the preparation of vat dyes of the types mentioned under α-isatinanilide.

5 : 7-**Dibromoisatin**—

(m.p. 248-250°)
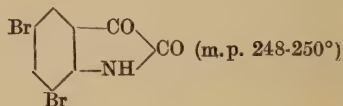
—is prepared by slowly warming isatin with bromine in concentrated sulphuric acid (G.P. 245042).

It yields a 5 : 7-**dibromoisatin chloride** (G.P. 237199), which is used for vat dyes of the types already described.

CHAPTER IV

BENZENESULPHONIC ACIDS

The Phenols and their Derivatives.

THE benzenesulphonic acids of technical importance are the monosulphonic acid and the *m*-disulphonic acid, since from these are obtained respectively phenol and resorcinol. Benzene is easily sulphonated with ordinary concentrated sulphuric acid at moderate temperatures, though the process is rather slow, because the solubility of benzene in sulphuric acid is very small. According to Martinsen (*Zeit. physik. Chem.*, 1907, **59**, 620), who studied the kinetics of the reaction, the speed of sulphonation of benzene is immeasurably great at 80°, and is complete almost in the same moment that the benzene goes into solution. If arrangements are made, as in G.P. 71556, for thoroughly intimate mixture of the two reactants, the sulphonation may be carried out at the ordinary temperature. This is done in the patented process by mixing together 1 part of benzene, 6 parts of concentrated sulphuric acid, and enough infusorial earth to make a shakeable paste. On allowing the mixture to stand for twenty-four hours at the ordinary temperature, complete sulphonation to the monosulphonic acid is obtained. The large excess of sulphuric acid required, however, makes the method unsuitable for technical use. The sulphonation of benzene is accelerated by the presence of sodium salts and certain other catalysts. Ambler and Cotton (*J. Ind. Eng. Chem.*, 1920, **12**, 968) found that a mixture of sodium sulphate and vanadium pentoxide doubled the rate of sulphonation.

As regards the formation of disulphonic acids, the decisive factor is temperature. Only very small amounts of disulphonic acids are formed at temperatures below 200°, and temperatures of 250° to 275° are required for complete disulphonation. Thus, no troublesome separations are required.

Benzenesulphonic acid :

The acid crystallises with $1H_2O$ in large colourless plates, which melt at 43° to 44°. The anhydrous acid melts at 65° to 66°. The sodium salt crystallises with $1H_2O$ in leaflets. 1 part of the salt is soluble in 1·75 parts of water at 30°.

Two processes are in use on the large scale for the sulphonation of benzene to the monosulphonic acid : (1) The ordinary sulphonation of benzene as liquid at or slightly above its boiling-point, (2) sulphonation of benzene as vapour at a much higher temperature. These will be described in turn.

1. Liquid Phase Sulphonation.

A detailed description of this process, as worked in this country during the War, is given in "Synthetic Phenol and Picric Acid," published by the Ministry of Munitions, from which the following summary has been made :

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(*a*) **Sulphonation.**—Benzene and sulphuric acid are mixed in the usual cast-iron sulphonation vessel, the proportion of acid used varying from 212 to 275 parts per 100 parts of benzene, and the strength of the acid varying between 95·3 per cent. and 100 per cent. The temperature at which the sulphonation is carried on depends on the plant in use. With sulphonators open to the atmosphere (and carrying, of course, reflux condensers) the temperature limit is the boiling-point of benzene, or 80°, but in some cases closed vessels are used, and the sulphonation worked at temperatures up to 120°, for the sake of quicker sulphonation. At 110° the sulphonation period is four to six hours, using an acid of 98 to 99 per cent. strength. In open vessels the rate of reflux of the benzene serves as a guide to the progress of sulphonation. When refluxing stops, the sulphonation is nearly complete, and the temperature may then be raised to 110° to complete the reaction. The disappearance of the benzene is not a sufficient indication of complete sulphonation, as benzene, though almost insoluble in sulphuric acid, is soluble to the extent of a few per cent. in concentrated sulphuric acid-benzenesulphonic acid solutions.

The proportion of sulphuric acid employed is such that when the benzene is completely sulphonated, the residual sulphuric acid is about 80 per cent. in strength. The amount of disulphonic acids formed is under 0·5 per cent. No sulphone is formed when 95 to 96 per cent. sulphuric acid is used, but in the French factories, which work with 100 per cent. acid, about 2 per cent. of sulphones, chiefly diphenyl-sulphone, $C_6H_5.SO_2.C_6H_5$, is obtained.

(*b*) **Isolation of Sodium Benzenesulphonate.**—The usual liming-out method may be used, after dilution of the melt with water, but to avoid forming a slimy calcium sulphate which would be difficult to filter and wash, it is necessary to keep the solution hot and to leave it faintly acid, when the calcium sulphate separates in a crystalline condition. The sodium sulphonate is then formed by addition of the exact quantity of sodium carbonate or sulphate to the filtrate and, after filtering from calcium carbonate or sulphate, sodium benzenesulphonate is obtained in almost quantitative yield on evaporating down the solution. The sulphonate may also be salted out by addition to the undiluted melt of 1·8 times its volume of saturated brine, though there is some loss of sulphonate by this method, since the salting out is not complete.

But in the complete process for the manufacture of phenol, considerable economy can be introduced by using the sulphite formed in the alkali fusion of the sulphonate to neutralise the acid of the sulphonation melt. This method was used at the Ellesmere Port factory during the War. The sulphonation melt is run into the aqueous sulphite solution (containing some phenol) and solid sulphite added to make up the necessary quantity. The temperature rises to about 100°. (Sulphur dioxide is given off, and this is used to neutralise the alkaline sodium phenate solution obtained from the fusion.) At the dilution used, the sodium sulphate formed separates almost completely, leaving the sodium benzenesulphonate in solution of 30 per cent. strength. The sodium sulphate is filtered off, the loss due to adhering sulphonate amounting to about 4 to 5 per cent. The filtrate is concentrated to 50 per cent. strength, and is then dried, if desired, by spraying the solution into a large brick chamber through which hot gases are passing. It was formerly the custom to dry the sulphonate

CHART IV.—BENZENESULPHONIC ACIDS AND PHENOL DERIVATIVES.
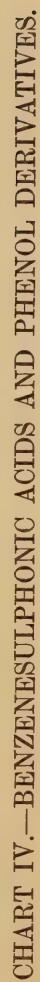
thoroughly before fusion, but it has been found that this is not necessary. Quite satisfactory results are obtained by running a concentrated solution of the sulphonate direct to the fusion pot. In fact, rather higher yields of phenol are obtained in this way, but this is more than offset by the fact that the fusion period is increased by about 50 per cent.

2. Vapour Phase Sulphonation.

The sulphonation of benzene in the form of vapour has been investigated by **Dr. Tyrer** in the United States, by Brunner, Mond and Co. in this country, and by Professor Guyot in France. Detailed results of these investigations are not available, but Dr. Tyrer has patented the process (U.S.P. 1210725), which is now used by the Bakelite Corporation of the United States in the course of their manufacture of phenol. A good account of this process is given by D. H. Killeffer (*J. Ind. Eng. Chem.*, 1924, **16**, 1066), to which reference should be made for plant details.

Benzene is vaporised at 10 to 12 lbs. pressure (in order to ensure the absence of liquid benzene on reaching the sulphuric acid) and the vapour led into ordinary concentrated sulphuric acid (66° Bé), which has been previously heated to 150°. The temperature of the acid is then gradually raised to 170° to 180°, while the benzene vapour is passed through at such a rate that some benzene escapes and condenses along with the steam also escaping. At the temperature mentioned, the rate of sulphonation of benzene is about ten times that obtained in liquid phase sulphonation in open vessels. Moreover, since the water formed in the reaction is carried off, sulphonation may be continued until almost all the sulphuric acid has been used up, thus leading to considerable economy, both of acid and of alkali to neutralise it afterwards. The course of the sulphonation is followed by noting the specific gravity of the mixture, which falls as the reaction proceeds. It has been found convenient to use up about 95 per cent. of the sulphuric acid, this point being indicated by the specific gravity of the mixture attaining 39° Bé. Some diphenylsulphone (about 2 per cent.) is always formed in this process, besides a rather higher proportion of disulphonic acids than is obtained in the ordinary sulphonation.

The reaction having been carried to the desired point, the sulphonation mixture is worked up by any of the methods already described. The custom at the Bakelite factory referred to is simply to neutralise the mixture with sodium carbonate solution so as to produce a hot 50 per cent. solution of the sulphonate, which is then run directly to the fusion pots. The small proportion of sodium sulphate present in the solution apparently causes little trouble in the fusion.

Phenol—

$$\underset{\bigcirc}{\text{OH}}$$

—forms long colourless prismatic crystals, m.p. 43°, b.p. 183°, D^{15} 1·066. It is soluble in 15 parts of water at ordinary temperature. At 84° it is miscible with water in all proportions.

When sodium benzenesulphonate is fused with caustic soda at a sufficiently high temperature, reaction occurs in accordance with the equation :

$$C_6H_5.SO_3Na \ + \ 2NaOH \ = \ C_6H_5.ONa \ + \ Na_2SO_3 \ + \ H_2O$$

In practice the melt can be successfully carried out with $2\frac{1}{2}$ molecular equivalents of alkali, though in some factories quantities up to 8 molecular equivalents are used. Caustic potash gives no better results than soda.

The caustic soda is melted in the usual iron fusion pot and the liquid raised to about 300°. While the replacement of the sulphonic acid group by hydroxyl can be effected at temperatures well below 300°, a convenient fluidity of the melt must be maintained, and if the minimum proportion of alkali is employed, temperatures of 300° and over must be used. It is important that the sulphonate should contain very little sodium sulphate, as this causes a serious thickening of the melt if present in quantity. The sulphonate is added gradually with constant stirring, while the temperature of the melt is slowly raised until, after the last of the sulphonate has been added, it reaches 340°, at which point it is maintained until the reaction is finished. The determination of the end-point is an empirical matter, arrived at by ascertaining the fusion period giving the best yield of phenol under the conditions employed. But a rough indication is given by cessation of frothing.

Oxidation by exposure to the air during fusion causes some loss of phenol. Nearly theoretical yields can be obtained by performing the fusion out of contact with air. On the other hand, experiments in which air was bubbled through during fusion gave yields less than the usual by 20 per cent. Sodium carbonate is the chief product of oxidation, with possibly some salicylate. However, under ordinary conditions, the loss by oxidation is small.

The sodium sulphite formed is practically insoluble in caustic soda and sodium phenate, and therefore separates in solid form without, however, having the effect of thickening the melt much. When the reaction is finished, the melt is run into such a quantity of water that the sulphite remains almost entirely undissolved in the strongly alkaline phenate solution formed, and is filtered off by means of a filter of fine nickel gauze, and washed with a little water, the washings being added to the filtrate. Some phenate persistently adheres to the sulphite. But this only causes loss of yield on the first working of the process if, as previously described, the sulphite is used in the neutralisation of the sulphonation mixture.

The phenol is now precipitated from the alkaline filtrate by acidification. The acid commonly used is sulphuric acid, but in the Ellesmere Port process, as already mentioned, the sulphur dioxide evolved in the neutralisation of the sulphonation mixture is used. Carbon dioxide is also an economical means of acidification, but in this case the conversion of sodium phenate to phenol is not complete, and a stronger acid must be added to finish the conversion. The phenol (containing some water in solution) separates as the upper liquid layer, and an aqueous solution of sodium sulphate, or sulphite, or carbonate, and some phenol, forms the lower layer. The two layers are separated. The phenol in the lower layer is either kept in circulation in the process by using this aqueous solution for dilution and neutralisation of the

6

sulphonation melt, or the phenol may be extracted with solvent naphtha or benzene.

The phenol is now distilled under reduced pressure.   The first runnings contain the water present, and on standing separate into two layers, of which the aqueous layer is used in the dissolving of the fusion melt, while the phenolic layer is returned to the still.   The distillation is controlled by testing samples for setting-point.   The phenol is collected when the setting-point reaches 39°.   The residues contain dihydroxydiphenols, diphenylene oxide, and tarry matter.

The overall yield of phenol from benzene is at best about 90 per cent., though usually under that figure.   The main loss occurs through side reactions during fusion of the sulphonate.

Phenol is used as a second component in azo dyes, mostly in conjunction with benzidine as first component, though other diamines are also used.   In the cases where benzidine is used, 1 molecule of diazotised benzidine is coupled with 1 molecule of phenol and with 1 molecule of another component.   The resulting dyes are generally too sensitive to alkalies to be useful as dyestuffs (though there are notable exceptions, such as Diamine Green B, etc.), and the hydroxyl group of the phenol nucleus is usually ethylated to overcome this defect.

Phenol is also used as intermediate for two triphenylmethane derivatives, Aurine and Phenolphthaleïn, which are likewise too sensitive to alkalies and are only employed as indicators.

A third general use of phenol is in the preparation of indophenols by oxidising a mixture of phenol and a *p*-diamine or *p*-aminophenol :

These indophenols are then used in making sulphur colours.

p-**Nitrosophenol**—
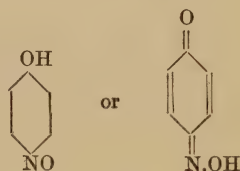
—crystallises in greyish-brown leaflets, which decompose at 124°.   It is moderately soluble in water, and easily soluble in alcohol, ether, and acetone, the solutions being pale green in colour.   It is sparingly soluble in glacial acetic acid.

The usual method of preparation is that described by Lange (" Die Schwefelfarbstoffe," 1911, p. 133).

94 kg. of phenol is dissolved in 1,000 litres of water and 85 kg. of concentrated caustic soda solution.   A solution of 75 kg. of sodium nitrite in 300 litres of water and 1,000 kg. of ice is added.   Cold dilute sulphuric acid, made from 235 kg. of concentrated sulphuric acid and 650 kg. of ice, is then added during one and a half hours, the

temperature being kept below 5°. The precipitated nitrosophenol is filtered off, centrifuged, and air-dried.

A modified method is described in E.P. 203060 (Siderfin, Tallentyre, Shannon, and Galbraith), in which nitrosation is accomplished by the gradual addition of water or ice to a sulphuric acid solution of nitrosylsulphuric acid. To 256 gms. of a solution of nitrosylsulphuric acid, containing the equivalent of 21·3 gms. of HNO_2 per 100 c.c., are added successively in small quantities 60 gms. of water or ice, 70 gms. of phenol liquefied with 10·5 gms. of water, and a further 120 gms. of water or ice. The temperature of the reaction mixture is kept at about 0°. The solution may then be diluted to precipitate the nitrosophenol, or it may be treated directly with carbazole derivatives to prepare carbazoleindophenols, which are required for the production of dyes of the Hydron Blue class.

The usefulness of p-nitrosophenol as an intermediate depends on its ability to form indophenols by condensation with bases, these indophenols being then used for the production of sulphur colours. The most notable example is the indophenol formed with carbazole—
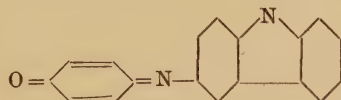
—which is used in making Hydron Blue.

o-**Nitrophenol**—
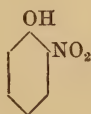
—crystallises in bright canary-yellow needles, m.p. 45°, b.p. 214°. It is volatile in steam. It is sparingly soluble in cold water, but dissolves in carbonate or caustic alkaline solutions giving a deep red solution.

p-**Nitrophenol**—

—crystallises in colourless needles, m.p. 114°, and is not volatile in steam. It is moderately soluble in hot water and very soluble in alcohol.

A mixture of these two nitrophenols is formed in about equal proportions when phenol is nitrated with 20 per cent. nitric acid at about the ordinary temperature. Sometimes an equivalent solution of sodium nitrate, to which sulphuric acid has been added, is used. In either case a large excess of reagent is used, about 1·8 molecules of HNO_3 to 1 molecule of phenol.

94 gms. of phenol, liquefied by addition of a little water, is dropped slowly into a well-stirred solution of 150 gms. of sodium nitrate in 400 c.c. of water and 250 c.c. of concentrated sulphuric acid, the temperature being kept below 20°. After stirring

for a further two hours, the liquid is allowed to stand, when the mixed nitrophenols separate as a dark heavy oil. The aqueous layer is decanted off and the nitrophenols washed free of acid by means of water containing a little chalk. Caustic soda must not be used, as this would resinify the crude nitrophenols. The o-nitrophenol is then distilled off with steam, and after allowing the distillate to stand several hours is filtered off. The yield is about 40 gms. From the residue p-nitrophenol is obtained by one or two extractions with boiling 2 per cent. hydrochloric acid. The filtrates from the extractions on cooling deposit the para-compound in long colourless needles, the yield being 40 gms.

A method by which only p-nitrophenol is obtained is described in G.P. 91314 (*Soc. Chim. des Usines du Rhône*). If phenol is first condensed with an aromatic sulphonyl chloride so as to form the phenyl ester of the sulphonic acid, on nitration of this ester the nitro group first enters the phenol nucleus in the para position. Thus using p-toluenesulphonyl chloride as cheapest, we get :

$$H_3C\langle\ \rangle SO_2.O\langle\ \rangle \longrightarrow H_3C\langle\ \rangle SO_2.O\langle\ \rangle NO_2$$
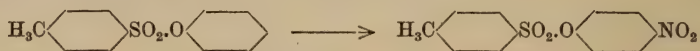
It is possible to hydrolyse this nitrophenyl ester to nitrophenol and sulphonic acid, but the temperature required is too high. If, however, the nitration is carried further so that a second nitro group enters (this time the toluene nucleus), the resulting dinitro derivative—

$$CH_3\langle\ \rangle SO_2.O\langle\ \rangle NO_2 \quad (O_2N)$$
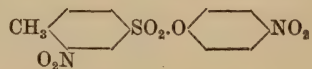
—can be hydrolysed with dilute caustic soda on the water-bath. The process is as follows :

100 kg. of phenol is dissolved in 1,000 litres of water and 42 kg. of caustic soda. The solution is warmed and 210 kg. of p-toluenesulphonyl chloride added gradually, and heating continued until the sulphonyl chloride has disappeared. The liquid is then cooled, the ester separated, well washed, and dried. It melts at 94° to 95°.

For the nitration, a finely powdered mixture of 100 kg. of the ester and 100 kg. of potassium nitrate is added gradually to 1,000 kg. of concentrated sulphuric acid, which is stirred and the temperature kept between 10° and 25°. When nitration is ended, the dinitro compound is filtered off, washed with water, and dried. It is obtained almost pure, and melts at 115°.

Hydrolysis is carried out by heating a suspension of 100 kg. of the dinitro body in a dilute aqueous solution of 30 kg. of caustic soda at about 100° until all has dissolved :

$$CH_3\langle\ \rangle SO_2.O\langle\ \rangle NO_2 \xrightarrow{+2NaOH} CH_3\langle\ \rangle SO_3Na + NaO\langle\ \rangle NO_2 \quad (O_2N)$$

On cooling, sodium p-nitrophenate crystallises out and is filtered off, and converted into the nitrophenol by acid. The yield is said to be quantitative.

Both *o*- and *p*-nitrophenol can be obtained by the action of caustic soda solution on the corresponding *o*- and *p*-nitrochlorobenzenes (pp. 2, 4), but although this is said to be the technical process of preparation, no details have been published.

Derivatives of *o*-Nitrophenol.

o-**Aminophenol—**

OH
NH₂
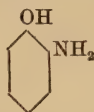
—crystallises when pure in colourless scales, but these soon become brownish-red in air. M.p. 174°. It can be sublimed. It is soluble in 59 parts of water at 0°, and rather more soluble in alcohol. Its hydrochloride crystallises in needles, soluble in 1·25 parts of water at 0°, and in 2·36 parts of alcohol.

It may be prepared from *o*-nitrophenol by reduction with sodium sulphide (Ullmann's " Enzyklopädie," vol. **9**, p. 47).

40 parts of crystalline sodium sulphide ($Na_2S.9H_2O$) is melted and heated to 125°, and at this temperature, while stirring, 10 parts of *o*-nitrophenol is added slowly, the temperature being gradually raised to 140°. The melt is at first red, but changes finally to light brown. It is diluted with water and filtered. The filtrate should be, at most, pale brown in colour. The aminophenol is precipitated by addition of sodium bicarbonate. The yield is 6·1 parts or 78 per cent.

The commercial product usually contains some aminophenazoxine, formed by condensation of 2 molecules of the aminophenol :

N
NH₂
: O
O
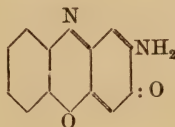
o-Aminophenol is used as a hair and fur dye, and also by condensation with 2 : 4-dinitrochlorobenzene yields a diphenylamine derivative used in making a sulphur colour.

o-**Nitroanisole—**

OCH₃
NO₂
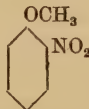
—a colourless oil at ordinary temperature. The solid melts at 9·4°, b.p. 273° (760 mm.), 150·5° to 151° (19 mm.), D_4^{20} 1·254.

The methylation of *o*-nitrophenol is carried out by means of methyl chloride. 139 parts of nitrophenol is dissolved in 400 parts of water containing 40 parts of caustic soda. 80 parts of sodium carbonate and 400 parts of methyl alcohol (90 per cent. will do) are added, and the solution cooled to 10° in an autoclave fitted with a stirrer. Methyl chloride is then added to the extent of 88 parts (1·75 mols.) and the autoclave heated at 100° for eight hours. The pressure developed is about 60 lbs.

After cooling the product is poured into water, the nitroanisole separated, and after washing with a little caustic soda solution to remove unchanged nitrophenol, then with water, is dried and distilled. The yield is over 80 per cent.

The alcohol used can, of course, be recovered and used again.

Another method of preparation is described on p. 13.

o-Nitroanisole can be reduced to o-anisidine by means of iron and a little hydrochloric acid, as in the preparation of aniline.

o-Anisidine—
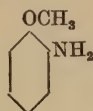
—a colourless oil at ordinary temperature, m.p. 2·5°, b.p. 225°, D_{15}^{15} 1·0978. Its acetyl derivative melts at 87° to 88°.

A modification of the ordinary method of reduction applied to o-nitroanisole is described by Heumann ("Die Anilinfarben," IV., i., 310).

o-Anisidine is used as a first component in azo dyes, to which it imparts unusual brightness of shade, due probably to the methoxy group in the o-position.

Dianisidine—

—crystallises from dilute alcohol in colourless leaflets, m.p. 137° to 138°, which become violet in air. It is fairly soluble in hot water, but sparingly in cold water, easily soluble in alcohol, ether, benzene, chloroform, and acetone. Its **hydrochloride** crystallises in prisms, easily soluble in water, but on boiling with water is partly dissociated, giving a sparingly soluble basic salt. The **sulphate**, $C_{14}H_{16}O_2N_2.H_2SO_4$, crystallises from water in short needles. 100 parts of water at 20° dissolve 1·12 parts of the sulphate and at 100° 4·17 parts. The **diacetyl** derivative forms colourless prisms, m.p. 231°.

Dianisidine is prepared by reduction of o-nitroanisole to hydrazoanisole and transformation of this in acid solution, the process being similar to that by which benzidine is prepared from nitrobenzene (p. 29) :
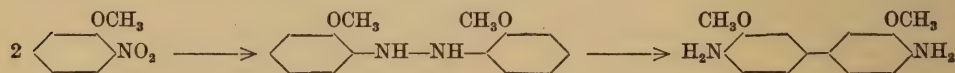
Very little information has been published with regard to the course of the successive reactions, in particular as to the final transformation. It is known, however, that there is no o-p-compound formed—that is, no diphenyline derivative, as in the preparation of benzidine. The only reaction which occurs besides the main one is a slight amount of fission of the hydrazoanisole with formation of o-anisidine.

A description of the manufacture of dianisidine, with some plant details, has been given by Jansen (*Zeit. für Farben-Ind.*, 1913, **12**, 247). For the plant details,

the original paper should be consulted. The essentials of the process are as follows :

30 kg. of *o*-nitroanisole, 40 kg. of zinc dust, and 20 kg. of alcohol are stirred and warmed until reduction begins, when a mixture of 14 kg. of alcohol and 4 kg. of 30 per cent. caustic soda is slowly added until the mixture has become pale grey. This requires about six hours. No temperature is mentioned. The mixture is then diluted with about 25 litres of water, 5 kg. of hydrochloric acid diluted with some water added, and finally another 340 litres of water. After allowing to settle, the mixture is filtered through wool, the hydrazoanisole remaining on the filter.

The hydrazo compound is then stirred into 173 kg. of sulphuric acid (arsenic-free), which has been previously diluted with about 220 litres of water and cooled to 48° to 50°. After stirring for five hours, the liquid is warmed during two hours to 60°, stirred two hours more at this temperature, and then raised to 90°. 2 kg. of zinc dust is added to decolourise the liquid, which should be yellowish, not brown. The liquid is filtered at 90°, 1 kg. of thiosulphate and 1 kg. of hydrochloric acid added, and then 250 kg. of hydrochloric acid, the whole being stirred for a few hours. It is then allowed to stand for two days, when it becomes thick with a crystalline precipitate, and this is filtered off through wool. The crystalline paste is stirred with 90 litres of hot water and heated till it dissolves, when the solution is filtered, the residue being boiled out with a further quantity of water. To the total filtrate, heated to boiling, 55 kg. of ammonia is added all at once, the mixture well stirred, and allowed to stand for two days. The precipitated dianisidine base is filtered off, washed with weak ammonia, then with very dilute caustic soda until the filtrate just reddens phenolphthaleïn. The yield is 20 kg. of base (about 83 per cent.).

The crude base obtained by some such method as this cannot conveniently be purified by vacuum distillation as can be done with benzidine. Too much decomposition occurs. A fair purification, however, can be obtained through the sulphate, formed by adding Glauber salt to a solution of the hydrochloride. The precipitated sulphate is washed with ice-cold water on the filter, and the base again obtained by stirring the sulphate with ammonia.

Dianisidine, like benzidine and tolidine, yields a tetrazo compound, which can be coupled with either two molecules of the same end component, or 1 molecule each of two different end components in succession. The resulting azo dyes are direct cotton colours, which are considerably bluer in shade than those derived from benzidine or tolidine, but otherwise show much the same properties with regard to fastness to light, washing, acids, etc. They are usually somewhat brighter than the corresponding benzidine dyes.

By nitration of the acetyl derivative of *o*-anisidine in glacial acetic acid solution, a mixture of two nitro derivatives is formed, which on hydrolysis yields the two nitroanisidines :

4-**Nitro**-2-**anisidine**—

$$OCH_3$$
$$NH_2$$
$$NO_2$$
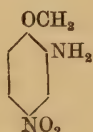
—orange needles (from water), m.p. 118°.   Acetyl derivative m.p. 131° to 132°.

5-**Nitro**-2-**anisidine**—

OCH₃
NH₂
O₂N
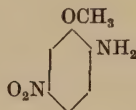
—m.p. 139° to 140°.   Acetyl derivative, m.p. 153° to 154°.

The proportions of the two nitro derivatives may be varied by variation of the temperature and other conditions.   Thus, as described in G.P. 98637 (Mulhouse) :

(1) 20 kg. of acet-*o*-anisidide may be added gradually to a stirred mixture at 10° of 120 kg. of nitric acid (38° Bé) and 100 kg. of glacial acetic acid.   The nitration is finished within a few minutes after the last of the acetyl compound has been added. The nitro compounds are precipitated by addition of water, filtered off, and washed with water.   In this way a mixture of 66 per cent. of 5-nitro- with 33 per cent. of 4-nitro-anisidine is obtained.

(2) 12 kg. of acet-*o*-anisidide may be nitrated with 200 kg. of nitric acid (41° Bé), the temperature being regulated between 25° and 40° so that no solid separates.   This procedure gives 75 per cent. of the 5-nitro- and 25 per cent. of the 4-nitro-anisidine.

The two nitro compounds are separated by the difference in basicity of the bases. The product of nitration is hydrolysed by heating with 40 to 60 per cent. sulphuric acid, the bases being precipitated with water and filtered off.   They are then dissolved in warm 25 per cent. sulphuric acid and, on adding water to the solution, the 5-nitro-anisidine is precipitated and may be filtered off.   The more strongly basic 4-nitro-anisidine is then precipitated from the filtrate by neutralising with alkali.

A modified form of this method of separation is given in G.P. 228357.   The mixture of the two nitroacetyl compounds is hydrolysed with warm 70 per cent. sulphuric acid.   Sufficient water is then added to reduce the acid to 40 per cent. On cooling, the sulphate of the 5-nitroanisidine crystallises out, while the filtrate on neutralisation yields the 4-nitro compound.

The nitroanisidines are used like *p*-nitroaniline for the production of dyeings on cotton by coupling their diazo compounds with *β*-naphthol or Naphthol AS.   The 4-nitro compound gives orange or scarlet shades, while the 5-nitro compound gives red or pink.

p-**Aminophenol**—

OH
NH₂

—crystallises in leaflets, m.p. 184°.   It dissolves in 90 parts of water and in 22 parts of alcohol at 0°.   It oxidises quickly in air.   Its solution in alkali is colourless at first, but rapidly becomes violet.   The **hydrochloride** is soluble at 0° in 1·4 parts of water. The **sulphate** is sparingly soluble in water.

Many different methods have been used or proposed for the preparation of *p*-aminophenol, but the most widely adopted are: (1) The reduction of *p*-nitrosophenol

with sodium sulphide; (2) reduction of *p*-nitrophenol with tin and hydrochloric acid (Paul, *Zeit. angew. Chem.*, 1896, **9**, 594), or with iron and hydrochloric acid (Paul, *loc. cit.*, 1897, **10**, 172); (3) electrolytic reduction of nitrobenzene (G.P. 295841, *Soc. Chem. Ind.*, Basle).

(1) According to Cain ("Intermediate Products, etc.," p. 118), *p*-nitrosophenol is dissolved in 30 parts of water containing some sodium sulphide, and a concentrated solution of 4 parts of crystalline sodium sulphide is added slowly until the yellow colour of the alkaline solution of nitrosophenol has disappeared. After cooling, the solution is made just acid with hydrochloric acid, the precipitate filtered off, extracted with boiling water, and the solution filtered, when, on cooling, *p*-aminophenol separates.

(2) The reduction of *p*-nitrophenol with iron and acid is carried out as follows : 250 parts of *p*-nitrophenol, 45 parts of concentrated hydrochloric acid, and 500 parts of water, are stirred in an iron reduction vessel fitted with a reflux condenser, and heated to 98°. About 400 parts of iron borings are added in lots of 15 to 20 parts at a time. After each addition an energetic reaction takes place, and this is allowed to subside before the next addition is made. The mixture is then brought to boiling-point, 50 parts more iron added, and boiling continued for half an hour to finish the reduction. After diluting with 2,000 parts of water, the solution is made just alkaline with 25 to 30 parts of soda ash, so as to precipitate dissolved iron. On filtering and cooling the filtrate, the *p*-aminophenol crystallises out. The yield is 140 parts or 71 per cent.

(3) The electrolytic reduction of nitrobenzene was first investigated by Gatter-mann (*Ber.*, 1893, **26**, 1847), who found that, while *p*-aminophenol was the main product, some aniline was also formed. Phenylhydroxylamine is supposed to be formed as an intermediate stage in the production of the aminophenol :
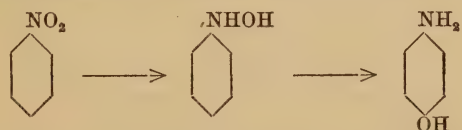
Using the conditions described in G.P. 295841, it is claimed that the proportion of aniline formed can be reduced to about 20 per cent. of the aminophenol. The vessel used for the electrolysis is a lead cylinder, and this serves as anode. The cathode is a hollow perforated copper cylinder, which is placed inside a porous cylinder standing in the lead vessel. Inside the copper cylinder is a stirrer, and one or more rods of lead dip into the cathode chamber. The anode chamber contains 30 per cent. sulphuric acid, and the cathode chamber is charged with 25 litres of dilute sulphuric acid (15° Bé) and 6 kg. of nitrobenzene. The mixture in the cathode chamber is kept emulsified by rapid stirring. At 80° to 95° a current of about 3 amperes per sq. dcm. of cathode surface at 3 to 3½ volts is passed until the nitrobenzene has disappeared. Milk of lime is then added, and the aniline distilled off with steam. The remaining solution of *p*-aminophenol is filtered hot from calcium sulphate and evaporated to crystallising point. The yield of *p*-aminophenol is about 56 per cent. of the

theoretical. The presence of arsenic in the sulphuric acid reduces the proportion of aniline formed to about 10 to 15 per cent. of the p-aminophenol.

p-Aminophenol serves chiefly as an intermediate for sulphur colours, either by heating it directly with sodium polysulphides or more commonly by first condensing it with 2 : 4-dinitrochlorobenzene to form 2 : 4-dinitro-4′-hydroxydiphenylamine (p. 6), which is then worked up for sulphur colours.

p-Aminophenol can be diazotised, and is used as first component in a few azo dyes.

p-**Nitrophenetole**—

—crystallises in prisms, m.p. 58°, b.p. 283°, D^{15} 1·18.

This is prepared by ethylation of p-nitrophenol with ethyl chloride in the same manner as o-nitroanisole is obtained from o-nitrophenol (p. 85). A yield of 90 per cent. is obtained.

p-**Phenetidine**—

—a colourless oil at ordinary temperature, m.p. 2° to 4°, b.p. 254°, D^{15} 1·0613. The **hydrochloride** melts at 234°, can be sublimed, and is easily soluble in water. The base is only slightly volatile in steam at 100°.

p-Phenetidine is prepared usually by reduction of p-nitrophenetole with iron and hydrochloric acid. An interesting variation of the usual reduction method is described by Ullmann (" Enzyklopädie," vol. **9**, p. 55).

To 100 kg. of water at about 6°, add slowly a mixture of 50 kg. of p-nitrophenetole and 50 kg. of iron borings, while simultaneously 7 kg. of hydrochloric acid is dropped in. At the beginning a few drops of 10 per cent. platinum chloride solution are added to the reaction mixture, which soon initiates a vigorous reaction. The reduction is finished in six to ten hours, as shown by a sample giving up no nitrophenetole to an ether extract. The base is then set free with soda, the liquid let settle for a few hours, the aqueous layer run off, and the remaining mass of borings and phenetidine after mixing with sawdust is extracted three times with toluene. On fractional distillation of the extract, a yield of 80 per cent. of phenetidine is obtained.

p-Phenetidine may also be prepared directly from phenol with the assistance of some of the previously prepared base, as described in G.P. 48543 (Riedel). The base is diazotised, coupled with phenol, the azo compound ethylated, and on reduction of the product two molecular proportions of p-phenetidine are formed in place of the one used to start with. The course of the reactions may be indicated thus :

$$EtO\langle\ \rangle N{:}N.Cl\ +\ \langle\ \rangle OH\ \longrightarrow\ EtO\langle\ \rangle N{:}N\langle\ \rangle OH$$

$$\xrightarrow[EtCl]{}\ EtO\langle\ \rangle N{:}N\langle\ \rangle OEt\ \xrightarrow[Reduction]{}\ EtO\langle\ \rangle NH_2\ +\ H_2N\langle\ \rangle OEt$$
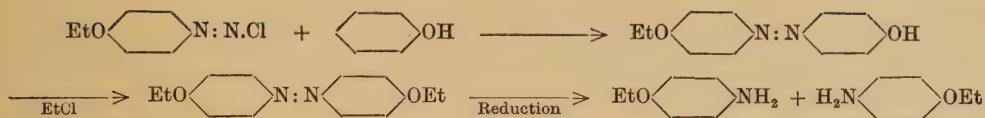
13·7 kg. of phenetidine, dissolved in 200 litres of water and 37·5 kg. of 20 per cent· hydrochloric acid, is diazotised in the usual way with 7 kg. of sodium nitrite dissolved in water. The solution of diazo compound is run into a solution of 9·5 kg. of phenol and 20 kg. of sodium carbonate in 350 kg. of water. The azo compound separates in quantitative yield as a brown precipitate, which may be crystallised from aqueous alcohol as small brown needles, m.p. 104° to 105°, soluble in caustic alkalies, alcohol, glacial acetic acid, etc.

The azo compound is ethylated by dissolving 10 kg. of it in 50 litres of alcohol and 1·66 kg. of caustic soda, adding 4·6 kg. of ethyl bromide and heating under pressure for ten hours at 150°. (Ethyl chloride or ethyl sodium sulphate may equally well be used for the ethylation.) The alcohol is distilled off, sodium bromide extracted with water, and any unchanged hydroxyazo compound with dilute caustic soda. The diethoxyazobenzene obtained crystallises from alcohol in lustrous yellow leaflets, m.p. 156°, which can be sublimed without decomposition. It is sparingly soluble in alcohol, but easily soluble in acetone and glacial acetic acid.

For the reduction 10 kg. of the diethoxy compound is warmed with 6 kg. of tin and 50 kg. of 20 per cent. hydrochloric acid. When all the diethoxy compound has disappeared owing to reduction and solution of the *p*-phenetidine formed from it, the solution is made alkaline and the phenetidine distilled in superheated steam.

The method works well and has been used on the manufacturing scale.

o-**Nitro**-*p*-**phenetidine** :

$$\begin{array}{c} OC_2H_5 \\ \langle\ \rangle NO_2 \\ NH_2 \end{array}$$
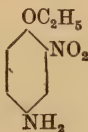
When acet-*p*-phenetidine (phenacetine) is nitrated with aqueous nitric acid, the nitro group enters the ortho position to the amino group, but if the nitration is carried out in sulphuric acid solution, the nitro group takes a position ortho to the ethoxy group. This latter compound is the more valuable of the two. Its preparation is given in G.P. 101778 (Meister Lucius and Brüning).

A solution of 18 parts of phenacetine in 80 parts of sulphuric acid (66° Bé) is nitrated at 5° with a mixture of 12 parts of nitric acid (36° Bé) and 12 parts of concentrated sulphuric acid. The nitro body is precipitated by pouring the reaction mixture on to ice, and is obtained as a light yellow precipitate. It is hydrolysed by dissolving in diluted sulphuric acid and heating for several hours at 80° to 90°. On cooling, the sulphate of the nitrophenetidine separates as a thick crystalline mass of reddish colour. It is purified by recrystallisation from hot water. The free base is obtained by addition of alkali as an orange-yellow oil, which solidifies on standing. It may be crystallised from dilute alcohol as yellow needles, m.p. 170°.

Like the nitroanisidines and other similar bodies this substance is used for dyeing on cotton by coupling its diazo compound with β-naphthol. It gives orange-yellow dyeings of good fastness.

Picric acid—
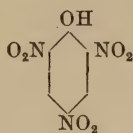
—crystallises in lemon-yellow prisms, m.p. 122·5°, sparingly soluble in water. It is still less soluble in water containing sulphuric acid, and is almost insoluble in 40 per cent. sulphuric acid. The sodium salt is readily soluble in water. The salts with lead and some other metals are rather dangerously explosive.

Picric acid may be prepared by the direct nitration of phenol (G.P. 126197, Gutensohn), but the tendency of the nitric acid to oxidise phenol (to oxalic acid, etc.) is so strong that this method is not usually employed. It has been found that a preliminary sulphonation of the phenol protects it in large degree from oxidation and in the subsequent nitration the sulphonic acid groups are displaced by nitro groups.
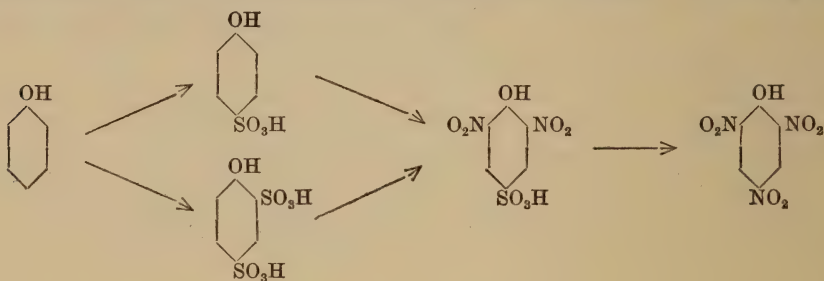
The nature and proportions of the intermediate sulphonic acids and nitrosulphonic acids depend on the conditions of sulphonation and nitration. Detailed investigations of the intermediate stages in the formation of picric acid by the ordinary process have been made by King (*J.C.S.*, 1921, **124**, 2105) and by Marqueyrol and collaborators (*Bull. Soc. Chim.*, 1919, **25**, 370; 1920, **27**, 140, 195, 370, 547).

There has been much variation of practice in carrying out the preparation of picric acid, especially in the degree of dilution used. Several different processes are described in the " Technical Records of Explosives Supply " (No. 6, Synthetic Phenol and Picric Acid), published by the Ministry of Munitions. That which allows of the most exact regulation of the reactions is the process in which strong acids are used throughout. It is carried out as follows : 30 lbs. of phenol is melted and run into an enamelled nitrating vessel provided with stirrer and steam-jacket. 3·5 molecular proportions of 94 per cent. sulphuric acid is added and the temperature raised to 100°. After two hours at this temperature, sulphonation equilibrium has been reached, and the solution is cooled to about the ordinary temperature.

The nitrating acid which is now run in has the composition :

H_2SO_4	..	..	..	..	..	..	57·5 per cent.
HNO_3	..	..	..	..	..	..	38·5 ,,
H_2O	..	..	..	..	..	..	4·0 ,,

—and the total quantity used contains 4·5 molecular proportions of nitric acid. Half of this quantity is first run in below 50° during about two hours. External cooling may be necessary at this stage. A mixture of mononitro- and dinitrosulphonic acids has been formed. Addition of the mixed acid is now stopped, and the temperature raised to 65° in order that all the nitric acid so far added may be used up. At 65°, the remaining half of the mixed acid is slowly added at such a rate that the heat evolved raises the temperature by 1° every three minutes until 80° is reached, when about three-quarters of the total acid has been added. The remainder of the acid may be added more quickly, so as to produce a regular rise of temperature, and so that when the last of the acid is run in the temperature has attained 115°. This temperature must be reached to complete the nitration, but at 115° nitration is very rapid and all the nitric acid is quickly used up. The mixture is allowed to cool to 100°, and is then cooled externally as quickly as possible to 25°. The picric acid formed crystallises out, and the mass is filtered through asbestos. After washing the picric acid with a little 75 per cent. sulphuric acid to remove adhering spent acid, the washing is continued with water. The yield of picric acid is 218 per cent. of the phenol used.

The spent acid contains 73 per cent. H_2SO_4, 0·65 per cent. HNO_3, 3·6 per cent. HNO_2, and 4·2 per cent. picric acid.

While formerly used as a dyestuff, its chief use in the dyestuff industry now is in the preparation of picramic acid.

Picramic acid—
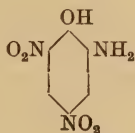
—crystallises in red needles, m.p. 168° to 169°. 100 parts of water at 22° dissolve 0·14 part, and in hot water it is readily soluble. It is dissolved both by alkalies and by acids giving in aqueous caustic soda a brownish-red solution, but in hydrochloric acid a colourless solution.

It is prepared from picric acid by reduction with sodium hydrogen sulphide (Brand, *J. pr. Chem.*, 1906 [2], **74,** 472). It is not necessary to prepare the sodium hydrogen sulphide previously; it may be formed in the reaction mixture by addition of a molecular proportion of hydrochloric acid to sodium sulphide.

229 gms. of picric acid is dissolved in 2 litres of water at 50°, with addition of 60 gms. of sodium carbonate. 400 gms. (1·6 gm.-mols.) of sodium sulphide crystals, $Na_2S.9H_2O$, dissolved in 750 c.c. of water, is run in slowly, and at the same time dilute hydrochloric acid, made from 155 c.c. of 30 per cent. hydrochloric acid and 500 c.c. of water, is added at about the same rate, the solution being well stirred. Stirring is continued for a further half-hour, and the solution then allowed to stand for twelve hours. Sodium picramate separates, and this is filtered off and washed with a little saturated salt solution. It is then dissolved in 3 litres of water, filtered, and the solution run into nearly boiling dilute acid, made from 120 c.c. of 30 per cent. hydrochloric acid and 700 c.c. of water. The solution is allowed to cool, when picramic acid

crystallises out, and is filtered off, washed with cold water, and dried. The yield is about 167 gms. or 84 per cent.

As an *o*-aminophenol derivative, picramic acid is used for the preparation of several afterchrome or metachrome wool colours by coupling its diazo compound with various phenolic compounds.

o-**Aminophenol**-*p*-**sulphonic acid** :

$$
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{SO}_3\text{H}
\end{array}
$$
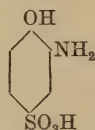
The acid crystallises in scales with $\frac{1}{2}$H$_2$O, sparingly soluble in cold water.

The preparation of this substance from *o*-nitrochlorobenzene-*p*-sulphonic acid has already been mentioned (p. 11). It may also be prepared as described in G.P. 93443 (*Soc. Chem. Ind.*, Basle) by sulphonating *o*-aminophenol.

100 parts of *o*-aminophenol are dissolved in 480 parts of sulphuric acid, 240 parts of 24 per cent. oleum added, and the solution heated at 90° to 95° for an hour. The aminophenolsulphonic acid may then be isolated in the usual way, after dilution, through the calcium and the sodium salt.

o-Aminophenolsulphonic acid can be diazotised, and is used as first component in a number of monoazo dyes, the second component being a *m*-diamine, or dihydroxy compound of the benzene or naphthalene series. These dyes are distinguished by the fastness to light, milling, and potting of their afterchromed shades.

2-**Nitro**-6-**aminophenol**-4-**sulphonic acid** :

$$
\begin{array}{c}
\text{OH} \\
\text{O}_2\text{N} \qquad \text{NH}_2 \\
\text{SO}_3\text{H}
\end{array}
$$
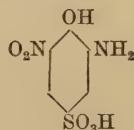
The acid crystallises in greyish-brown prisms, sparingly soluble in cold, but easily in hot water, giving reddish-yellow solutions. The potassium salt is sparingly soluble in cold water.

The preparation of this substance is given in G.P. 93443, quoted above, starting from *o*-aminophenol. When the sulphonation is complete, the solution is cooled to 0° and nitrated directly at 0° to 3° with a mixture of 58 parts of nitric acid and 116 parts of sulphuric acid. After standing for two hours the solution is poured on ice and the precipitate filtered off and pressed. It is purified by dissolving it in 400 parts of boiling water and allowing to crystallise.

A much purer product is claimed by Hillyer and the National Aniline Co. (U.S.P. 1504044), who find it preferable to isolate the *o*-aminophenolsulphonic acid before nitrating. 100 parts of pure dry *o*-aminophenol-*p*-sulphonic acid is dissolved in 300 parts of sulphuric acid (66° Bé). Very little heat is developed. The solution is cooled to $-5°$ and nitrated with a mixed acid composed of 29 to 30 per cent. HNO$_3$, 65 per cent. H$_2$SO$_4$, and 5 per cent. H$_2$O, sufficient of the mixed acid being taken to

contain 34 parts of HNO_3. The temperature during nitration is kept below $0°$. After stirring for two to three hours, the solution is poured on to 500 parts of ice. The product partly separates as solid. The total yield is 80 to 90 per cent., about 65 to 75 per cent. being as solid and 15 to 30 per cent. in solution. The whole may be brought into solution, and used directly for azo colours, by nearly neutralising with alkali.

Starting from phenol itself, the substance may be prepared, as in G.P. 121427 (Badische), by sulphonating to the p-sulphonic acid, nitrating to the 2 : 6-dinitro compound and partially reducing this :

$$\text{OH} \longrightarrow \text{OH, SO}_3\text{H} \longrightarrow \text{O}_2\text{N}-\text{OH}-\text{NO}_2, \text{SO}_3\text{H} \longrightarrow \text{O}_2\text{N}-\text{OH}-\text{NH}_2, \text{SO}_3\text{H}$$
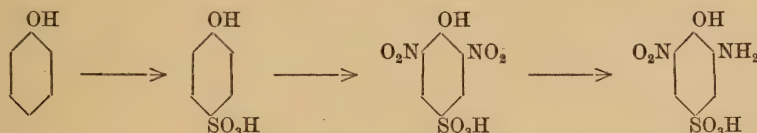
Phenol (10 parts) is sulphonated with 13 parts of sulphuric acid at $100°$ to $110°$. The solution is then cooled and poured into 100 parts of water. The nitration is carried out by adding 40 parts of 62 per cent. nitric acid, and heating the mixture to boiling till a sample on cooling deposits crystals of dinitrophenol. The solution is then cooled, filtered from dinitrophenol, and the 2 : 6-dinitrophenol-4-sulphonic acid isolated as the yellow crystalline potassium salt by adding 10 parts of potassium carbonate. After dissolving 30 parts of this salt in 300 parts of hot water, the solution is cooled and 200 parts of ammonium sulphide added. Reduction takes place with a slight development of heat, and is complete in two to three hours. The product is isolated, either as acid by adding hydrochloric acid, or as potassium salt by acidifying with acetic acid and adding potassium chloride.

2 : 6-Diaminophenol-4-sulphonic acid :

$$\text{H}_2\text{N}-\text{OH}-\text{NH}_2, \text{SO}_3\text{H}$$
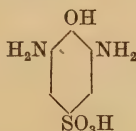
The acid crystallises in white leaflets, soluble in water, the solutions becoming brown by air oxidation.

It is prepared by reducing 2 : 6-dinitrophenol-4-sulphonic acid (above) with zinc dust and hydrochloric acid (G.P. 148212, Meister Lucius and Brüning). The solution obtained is usually employed directly in making azo dyes, but the sodium salt can be isolated by addition of sodium acetate and the necessary common salt.

This diaminophenolsulphonic acid yields a yellow tetrazo compound which, coupled with two molecular porportions of β-naphthol or Schäffer acid, gives disazo dyes. These are wool colours which can be afterchromed to produce fast black shades.

Salicylic acid :

$$\text{OH}-\text{COOH}$$
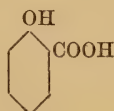
The acid crystallises from water in needles, m.p. 158·5°. The following table gives the solubility of the acid in water expressed as grams of acid in 1,000 gms. of solution (Savarro, *Atti R. Accad. Sci. Torino*, 1913, **48**, 455) :

0°	..	.. 1·24	35°	..	.. 3·51	70°	..	.. 13·70
5°	..	.. 1·29	40°	..	.. 4·16	75°	..	.. 17·55
10°	..	.. 1·35	45°	..	.. 4·89	80°	..	.. 22·09
15°	..	.. 1·84	50°	..	.. 6·38	85°	..	.. 27·92
20°	..	.. 2·00	55°	..	.. 7·44	90°	..	.. 37·35
25°	..	.. 2·48	60°	..	.. 9·00	95°	..	.. 50·48
30°	..	.. 2·98	65°	..	.. 10·94	100°	..	.. 75·07

At 18·2° it dissolves in 172 parts of benzene, in 2·5 parts of 90 per cent. alcohol, in 2 parts of ether, and in 80 parts of chloroform. Its sodium salt is soluble in water and in alcohol.

It is prepared by the action of carbon dioxide on sodium phenate. As originally described in Kolbe's patent G.P. 426, carbon dioxide was brought into contact with sodium phenate at 180° to 200°. This procedure gave at most a 50 per cent. yield of salicylic acid, the reaction product containing always considerable quantities of phenol. The reason for this was pointed out by Schmitt, who showed that the reaction under Kolbe's conditions was in effect as follows :

$$2C_6H_5.ONa + CO_2 \longrightarrow C_6H_4 \Big\langle {\overset{ONa}{\underset{COONa}{}}} + C_6H_5.OH$$
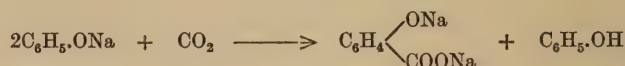
Schmitt further proved that at much lower temperatures phenol could form, by addition with carbon dioxide, a carbonate which at 120° to 145° was transformed by intramolecular change into salicylic acid :

$$C_6H_5.ONa + CO_2 \longrightarrow C_6H_5.O.COONa \longrightarrow C_6H_4 \Big\langle {\overset{OH}{\underset{COONa}{}}}$$
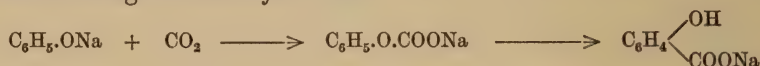
His improved process (G.P. 29939), therefore, consisted in passing carbon dioxide into sodium phenate at about the ordinary temperature until phenyl sodium carbonate was completely formed, and then heating this at 120° to 145° to effect the transformation to salicylic acid. Incidentally, it was shown that an essential condition for the formation of phenyl sodium carbonate was absolute dryness of the sodium phenate, which necessitated heating the latter in a high vacuum at 150° to 160°. Later it was shown by Heyden (G.P. 38742) that it was not necessary to cool the dried phenate to ordinary temperature in order to form phenyl sodium carbonate. The formation of the carbonate could be carried out at such a temperature (120° to 145°) that its transformation to salicylate would immediately follow, it being only necessary to avoid such a temperature (above 145°) as would bring Kolbe's reaction into play, with partial formation of phenol. The preparation is, therefore, carried out as follows :

Pure phenol is used, whose setting-point is not below 39°, and which does not redden on fusion. It is stirred into an equimolecular quantity of caustic soda (free from carbonate) dissolved in a little water. The phenol dissolves and the solution is now heated in an autoclave with powerful stirring gear under high vacuum so as to evaporate the sodium phenate to dusty dryness, the temperature being ultimately

raised to about 160°. Grinding of the phenate to fine powder is facilitated by having a number of heavy balls in the autoclave.

The autoclave is now cooled to 100° and carbon dioxide, free from moisture, carbon monoxide, or sulphur compounds, is passed in, with constant stirring. The carbon dioxide is quickly absorbed at first, with development of heat, and the temperature must not be allowed to rise above 145°. Later, absorption slows off somewhat and the pressure of the carbon dioxide in the autoclave is maintained at 5 to 6 atmospheres until the end of the reaction, which is indicated by a simultaneous fall of temperature and rise of pressure due to non-absorption of the carbon dioxide now being forced in. After cooling and blowing off excess of carbon dioxide, the salicylate is dissolved in the minimum quantity of water, giving a yellow solution from which it is precipitated by addition of hydrochloric acid.

As thus obtained, the product contains some impurities, which, according to G.P. 65131 (Hofmann), can be removed by adding stannous chloride solution to the hot solution of salicylate until the liquid becomes water-white. The tin is precipitated as $SnO(OH)_2$. This is filtered off and the salicylic acid precipitated from the filtrate by acid.

It may be further purified by distillation with superheated steam at 140°.

The yields obtained on the manufacturing scale approximate to the theoretical.

Salicylic acid is used very largely as a second component in all classes of azo dyes from mono- to tetrakisazo. Two molecules of a diazo compound can be coupled with 1 molecule of salicylic acid, one in the *para* position, and one *ortho* to the hydroxyl group, but only one or two of the azo dyes made from it are of this nature. All the monazo dyes derived from salicylic acid are yellow or orange in shade, and in most of the others the shades vary between yellow and brown. To all these dyes, but especially to the mono and disazo dyes, salicylic acid imparts the property of dyeing on chromemordanted wool or the capability of being afterchromed.

A few dyes of the triphenylmethane series are derived from salicylic acid by condensation with formaldehyde, Michler's hydrol, etc. These also are chrome wool colours.

In the anthraquinone series a yellow lake pigment is made by condensing salicylic acid with α-aminoanthraquinone to form the anthraquinonylamide of salicylic acid.

Aminosalicylic acid :
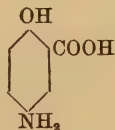
This substance may be prepared from salicylic acid by nitration, which yields a mixture of the 3- and 5-nitrosalicylic acids—

7
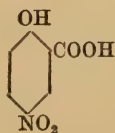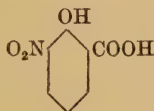
—followed by reduction of the 5-nitro derivative as described by Hirsch (*Ber.*, 1900, **33,** 3239) and Hübner (*Ann.*, 1879, **195,** 6). But a simpler method, which avoids production of isomers, is to couple a suitable diazo compound with salicylic acid and reduce the azo compound formed.

As described by Fischer and Schaar-Rosenberg (*Ber.*, 1899, **32,** 81), 500 gms. of aniline hydrochloride is dissolved in 600 gms. of hydrochloric acid (D 1·19) and 3,000 gms. of ice, the mixture showing a temperature of $-20°$. This is diazotised by a solution of 290 gms. of sodium nitrite in 1 litre of water. When diazotisation is complete (in about fifteen minutes), the solution is run into a solution of 533 gms. of salicylic acid and 2,200 gms. of soda crystals in 10 litres of water. The azo compound separates as the yellow sodium salt, and this is filtered off and washed with a little water.

It is now reduced either with stannous chloride, as used by the above mentioned authors, or better with sodium hydrosulphite ($Na_2S_2O_4$) as recommended by Grand-mougin (*Ber.*, 1906, **39,** 3930). In the latter case, the azo compound is stirred into 10 litres of boiling water, the mixture made alkaline with caustic soda solution, and sodium hydrosulphite added till reduction is complete, as shown by the disappearance of the colour of the azo compound. About 1,350 gms. of sodium hydrosulphite powder are required. The aniline formed is distilled off with steam, leaving a solution of sodium aminosalicylate, which may either be used directly for azo dyes or the aminosalicylic acid may be precipitated by acidification.

Aminosalicylic acid can be diazotised, and is used as a first component in a series of disazo dyes in which its diazo compound is coupled with α-naphthylamine or Cleve's acids as middle component, the last component being a naphtholsulphonic acid or dihydroxynaphthalenesulphonic acid. In this way, wool colours are obtained which, by afterchroming, yield very fast blacks and greens. Aminosalicylic acid is also used in making chrome colours of the triphenylmethane class by condensation with Michler's hydrol and similar bodies.

Benzene-*m*-disulphonic acid :

$$\begin{array}{c} \text{SO}_3\text{H} \\ \hexagon \\ \text{SO}_3\text{H} \end{array}$$
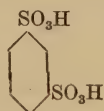
The sodium salt crystallises with $4H_2O$.

Sulphonation of benzene to the disulphonic acids takes place at temperatures of over 200°. The product is almost entirely the *m*-disulphonic acid, under ordinary conditions only about 1 per cent. of the *p*-disulphonic acid being formed. However, if heating be continued for a long time past the point of complete disulphonation, or if mercury salts are present during sulphonation, some of the *m*-acid is transformed into *p*-acid, an equilibrium mixture of the two acids in the proportion of 2 : 1 being ultimately attained. Since both acids yield resorcinol on fusion of their sodium salts with caustic soda, the separation of the acids is not a matter of technical importance.

Manufacturing methods of preparation of benzenedisulphonic acid (and of resorcinol from it) are described by Bindschedler and Busch (*Mon. Sci.*, 1878, 1169), Schoop

(*Zeit. Chem. Ind.*, 1887, **2**, 1), and Mühlhäuser (*Dingl. Polytech. J.*, 1887, **263**, 154). As described by the last-mentioned, the preparation is as follows:

(*a*) **Monosulphonation.**—60 kg. of benzene and 300 kg. of sulphuric acid (67° Bé) are well stirred and heated at 80° for ten hours, under a reflux condenser.

(*b*) **Disulphonation.**—The reaction mixture having been transferred to a larger sulphonation pot, 85 kg. of dry powdered sodium sulphate are added, and the mixture gradually heated during four hours to 225°, at which temperature it is maintained for a further eight hours. While rising in temperature, some benzene distils off and sulphur dioxide is evolved.

After cooling the solution is run into 1,500 litres of water, the hot solution neutralised with slaked lime made from about 200 kg. of lime, and after adding 800 litres of cold water to make the gypsum easier to filter, the mixture is filtered. The gypsum is boiled up with another 1,500 litres of water and again filtered off. The united filtrates are concentrated to about half the volume, and sufficient soda (6 to 10 kg.) added to convert the calcium into the sodium salt. The calcium carbonate is filtered off, and the solution of the sodium salt evaporated to dryness, and finely powdered. The yield of dry sodium salt is about 200 kg., or rather under 90 per cent.

The preparation of benzenedisulphonic acid from the monosulphonic acid has been studied in detail by Senseman (*J. Ind. Eng. Chem.*, 1921, **13**, 1124) with a view to obtaining the highest possible yield. The best results were obtained by heating the monosulphonic acid at 250° for one hour with about 150 per cent. excess of 95 per cent. sulphuric acid. A sodium salt or vanadium pentoxide was added as catalyst, the amount used being about 0·1 per cent. of the weight of acid taken. In this way yields of about 92 per cent. were obtained.

Resorcinol—
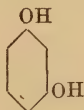
—crystallises in colourless prisms, m.p. 119°, b.p. 276·5°, or, under 16 mm. pressure, 178°. D^{15} 1·2717. On standing in air, it becomes pink and then brown, due to the action of ammonia. 100 parts of water at 0° dissolve 86·4 parts of resorcinol, at 12·5° 147·3 parts, and at 30° 228·6 parts. It is also very soluble in alcohol and ether, but sparingly soluble in cold benzene, 1 gm. dissolving in 435 gms. of benzene at 24°. It is almost insoluble in chloroform and carbon disulphide. Its aqueous solution gives a dark violet colour with ferric chloride. With bromine a precipitate of tribromoresorcinol is formed. This reaction is used in its estimation (Pence, *J. Ind. Eng. Chem.*, 1911, **3**, 820).

Resorcinol results in normal fashion from the fusion of the sodium salt of benzene-*m*-disulphonic acid with caustic soda. References to methods of manufacture have been given under benzenedisulphonic acid above. In the process described by Mühlhäuser (*loc. cit.*), the dry sulphonate is added gradually to twice its weight of caustic soda, which has been fused with a little water and raised to a sufficiently high temperature. The temperature is not specified, but is such that the sulphonate

dissolves quickly with a hissing noise. Heating is continued with stirring until the foaming dies down and the melt becomes oily in appearance and begins to turn brown. It is then poured on iron plates and allowed to solidify. The broken up cakes are dissolved in about twice the weight of water and the solution made just acid to litmus by addition of concentrated hydrochloric acid, sulphur dioxide being given off. The resorcinol is then extracted with amyl alcohol four times, the amyl alcohol distilled off with steam, and the residual aqueous solution of resorcinol evaporated to dryness in an enamelled pan. The yield of crude resorcinol from 125 parts of disulphonate is 28 to 29 parts. For purification it is distilled at first under ordinary pressure until some water and phenol come off, then under about 100 mm. pressure. The yield of pure distilled resorcinol is 20 to 23 parts. This corresponds to about 42 to 48 per cent. on the disulphonate, or an overall yield of 38 to 43 per cent. calculated on the original benzene.

An investigation has been made by Phillips and Gibbs (*J. Ind. Eng. Chem.*, 1920, **13,** 857) of the best conditions for the fusion of the disulphonate to resorcinol. They obtained the highest yields of resorcinol by fusing the disulphonate with 14 to 16 molecular proportions of caustic soda at 310° for two hours. Generally, a few per cent. of disulphonate remained unchanged under these conditions. Addition of water to the melt caused a considerable decrease in yield. The yields obtained were about 60 to 63 per cent., but this figure represents the total proportion of resorcinol formed, as estimated by the bromine method, and not the resorcinol actually isolated in pure condition.

Resorcinol is used as an end component in azo dyes. It couples very readily with diazo compounds, and it is possible to couple 2 molecules of a diazo compound, in succession, with 1 molecule of resorcinol, the resulting disazo dyes having the constitution :
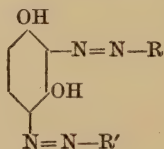
The azo dyes containing resorcinol as a component, like those containing *m*-phenylene-diamine, are brown in shade.

Resorcinol is also condensed with phthalic anhydride to produce Fluorescein, and through this the various dyes of the Eosin and Rhodamine types.

By condensation with *p*-nitrosodimethylaniline hydrochloride (on the fibre) it yields an oxazine dye.

Amidation of Resorcinol.

The hydroxyl groups of resorcinol may be replaced either singly or together by amino or substituted amino groups by the action of ammonia or an amine. The reaction is facilitated, like the corresponding reaction with the naphthol derivatives, by the use of sulphites of the amines in addition to the free amine. That is, the Bucherer reaction (p. 139) applies.

m-**Aminophenol** may be prepared, according to G.P. 49060 (Leonhardt), by heating 10 parts of resorcinol with 6 parts of ammonium chloride and 20 parts of 10 per cent. ammonia for twelve hours at 200° in an autoclave. The product is acidified with hydrochloric acid, any unchanged resorcinol extracted with ether, and the aqueous solution neutralised with sodium carbonate and evaporated to crystallising point. The *m*-aminophenol thus obtained is said to be completely air-stable.

No doubt the use of ammonium sulphite would enable the reaction to proceed at a lower temperature.

Dimethyl-*m*-**aminophenol** has been made, according to E.P. 18726 of 1900 (Badische), by heating 250 parts of resorcinol with 2,500 parts of 20 per cent. dimethylamine sulphite solution, and 400 parts of 30 per cent. dimethylamine solution in an autoclave at 125° until the resorcinol has disappeared, or nearly so. The liquid is then made alkaline with caustic soda or carbonate, and the excess dimethylamine driven off by steam. After acidifying the remaining solution with hydrochloric acid and boiling off sulphur dioxide, on evaporating to dryness the hydrochloride of dimethyl-*m*-aminophenol is obtained.

The other alkyl-*m*-aminophenols may be obtained in a similar manner.

According to E.P. 168689 (B.D.C., Green, and Brittain), the reaction can be made to proceed further, at any rate in the case of the monoalkylamines, so as to form symmetrical dialkyl-*m*-phenylenediamines. Thus, *e.g.*, *sym.* **Dimethyl**-*m*-**phenylenediamine**—

$$\underset{\text{NHCH}_3}{\overset{\text{NHCH}_3}{\bigcirc}}$$
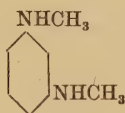
—is prepared by heating 55 parts of resorcinol with 66 parts of 35 per cent. methylamine sulphite solution and 125 parts of 25 per cent. methylamine solution in an autoclave at 125° for twelve hours. The product is made alkaline, and the excess of methylamine distilled off. The residue is acidified with hydrochloric acid, and any unchanged resorcinol extracted with ether. On now making the aqueous solution slightly alkaline with caustic soda, the dimethyl-*m*-phenylenediamine may be extracted with ether. It is finally purified by distillation *in vacuo* (b.p. 170° under 10 mm.). The yield is 67 per cent.

Monomethyl-*m*-**aminophenol** is formed as a by-product to the extent of about 5 per cent.

THE NITROTOLUENES AND THEIR DERIVATIVES

THE nitration of toluene is carried out in the same manner as that of benzene (Chap. II.). Complications arise, however, in the case of toluene owing to the greater number of possible isomers, and to the fact that the methyl group may be oxidised to some extent during the process, producing benzoic acids and even, in extreme cases, to tetranitromethane. By-products of this kind, however, are not of serious account in a carefully conducted nitration. For the manufacture of dyestuff intermediates, only the mononitrotoluenes and the 2 : 4-dinitrotoluene are of importance.

Mononitrotoluenes.

Nitration of toluene with one molecular proportion of nitric acid yields invariably a mixture of the three isomers in which the o- and p-compounds predominate. Holleman and his collaborators (*Rec. trav. chim.*, 1909, **28**, 408; 1914, **33,** 1) found that, using nitric acid alone (D 1·475, or 84 per cent.), the proportions of the isomers obtained at different temperatures remained nearly constant, as indicated in the following table :

Temperature.	Per Cent. Ortho.	Per Cent. Meta.	Per Cent. Para.
0°	56·0	3·1	40·9
30°	56·9	3·2	39·9
60°	57·5	4·0	38·5

The use of mixed acid causes a noticeable change in the proportions to about 63 per cent. o-, 2 per cent. m-, and 35 per cent. p-compound. But, using mixed acid, these proportions again remain fairly constant over a wide range of temperature and composition of the mixed acid.

The mononitration of toluene can be carried to completion with a more dilute mixed acid and at a lower temperature than that required for benzene. A mixed acid of the approximate composition—

$$HNO_3 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad 25 \text{ per cent.}$$
$$H_2SO_4 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad 55 \quad ,,$$
$$H_2O \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad 20 \quad ,,$$

—is used, 230 parts of this mixture being taken for the nitration of 100 parts of toluene. The nitration is carried out at 30°. In other details, the procedure is the same as that used for benzene. The yield of mixed nitrotoluenes is 140 to 142 parts from 100 parts of toluene.

The separation of the isomers is accomplished by a combination of repeated fractional distillation *in vacuo* and crystallisation, like that described for the separation of o- and p-nitrochlorobenzenes (p. 2). The first fraction consists mostly of

CHART V.—NITROTOLUENES AND THEIR DERIVATIVES.

the *o*-compound, and on cooling the residue to about 0° much of the *p*-compound crystallises out and can be separated from the oil by the centrifuge. The whole process of separation requires a special apparatus and technique which cannot be described here. Finally, most of the *o*- and *p*-compounds are separated in a pure state, but a residual middle fraction is obtained in which the *m*-compound has accumulated until it has reached a substantial proportion. Apparently it has been found possible to separate *m*-nitrotoluene from this residue, or to separate *m*-toluidine from the reduced mixture, since a few dyes have appeared on the market in which *m*-toluidine figures as an intermediate. But no information has been published on this point.

Methods have been patented for the isolation of the *o*-compound by subjecting the mixture to the action of reagents which attack only the *m*- and *p*-compounds. Alkaline arsenite at 130° to 150° under pressure reduces the *m*- and *p*-compounds to azoxy and amino derivatives, leaving *o*-nitrotoluene unchanged (G.P. 78002). The Clayton Aniline Co. proposed in G.P. 92991 to heat the nitrotoluenes with the sulphide residues from the Leblanc soda process, thereby converting the *m*- and *p*-compounds to the amines and leaving the *o*-isomer unchanged. However, the high efficiency of modern distillation apparatus renders such processes unnecessary.

o-**Nitrotoluene** is a liquid at ordinary temperature. It exists in two modifications, the labile α-form having a melting-point given by various observers as from − 9° to − 10·56°. The stable β-form melts at − 3·6°. The boiling-point is 220·4° (760 mm.). D_{15}^{15} 1·1643. It is volatile in steam, 30 gms. of *o*-nitrotoluene distilling with 1 kg. of steam at 100°.

p-**Nitrotoluene** forms colourless rhombic crystals, m.p. 54·5°, b.p. 237·7° (760 mm.), D 1·23.

m-**Nitrotoluene.**—M.p. 16°, b.p. 230°.

2 : 4-**Dinitrotoluene**—
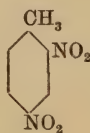
—needle-shaped crystals (from water), m.p. 71°, $D^{70\cdot5}$ 1·3108. Sparingly soluble in cold alcohol and ether, easily soluble in benzene.

This product is manufactured in the same way as *m*-dinitrobenzene (p. 18). Toluene is nitrated first to the mixture of mononitrotoluenes, using a mixed acid of the same composition as that used with benzene. This acid is more concentrated than is necessary, and probably to a small extent causes formation of dinitrotoluenes at this stage, but this is immaterial. The spent acid having been separated, fresh mixed acid of the same composition as that used for dinitrobenzene is run into the mononitrotoluenes at 115°. The product is worked up as described under dinitrobenzene. A detailed account of the process is given by Kayser (*Zeit. Farbenind.*, 1903, **2**, 16, 31).

As by-products a little of the 2 : 6- and traces of the 2 : 3-dinitrotoluenes are formed.

The yield obtained from 100 parts of toluene is 175 to 180 parts of dinitrotoluene or 90 to 93 per cent.

A. Derivatives of o-Nitrotoluene.

o-**Toluidine**—

CH_3
NH_2
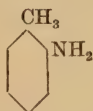
—a colourless liquid at ordinary temperature, b.p. 198·1° (760 mm.), D_{20} 0·9986, D_{15}^{15} 1·0031.   It exists in two forms, one of which freezes at − 21°, the other at − 15·5°. It is almost insoluble in water.   It is volatile in steam, 34 gms. of *o*-toluidine distilling with 1 kg. of steam.

The **hydrochloride,** $C_7H_9N.HCl+H_2O$, forms thick transparent crystals, m.p. 214·5° to 215°, soluble in water and alcohol.

The **sulphate,** $(C_7H_9N)_2.H_2SO_4$, crystallises in needles, moderately soluble in water. **Acetyl** derivative, m.p. 110°.

o-Toluidine is prepared by reduction of *o*-nitrotoluene in the usual way (p. 26).

It is used as a first component in a number of monazo dyes, and also, in one disazo dye, Brilliant Crocein 9B, as middle component.   It forms part of the mixture of bases used in the preparation of Magenta.   It is used in the preparation of an acid Rhodamine colour by condensation with fluorescein chloride and subsequent sulphonation.   *o*-Toluidine also takes part in the formation of several azine and thiazine dyes, by oxidising mixtures of it with *p*-diamines or thiosulphonic acid derivatives of *p*-diamines.   A dimethylindigo is made from it by condensation with chloroacetic acid and alkali fusion of the resulting *o*-methylphenylglycine.

o-**Toluidinesulphonic acid :**

CH_3
NH_2
HO_3S
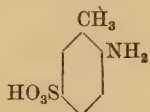
The acid crystallises with $1H_2O$ in prisms, sparingly soluble in cold water, but much more soluble in hot water.   The sodium salt crystallises with $4H_2O$.

This substance is prepared by heating *o*-toluidine acid sulphate, $C_7H_9N.H_2SO_4$, at 200°, following the process used in preparing sulphanilic acid from aniline (p. 57).

It is used as a first component in a few monazo dyes, particularly in conjunction with β-naphthol and with phenylmethylpyrazolone as second components.

Aminoazotoluene—

CH_3 CH_3
$-N=N-$ NH_2
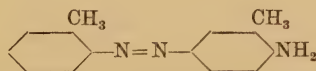
—crystallises in dark yellow leaflets or in short red prisms with a blue reflex, m.p. 100°. The base is almost insoluble in water, but is soluble in alcohol.   The hydrochloride forms orange yellow tables, sparingly soluble in cold water.

Aminoazotoluene is prepared from *o*-toluidine by the same procedure as that used in making aminoazobenzene from aniline (p. 62).

Aminoazotoluene is sulphonated to form a yellow wool dye. It is diazotised and coupled with various α- and β-naphtholsulphonic acids, thus forming red wool dyes, known as Cloth Reds. By reduction of aminoazotoluene a mixture, in equimolecular proportions, of *p*-tolylenediamine, and *o*-toluidine is obtained which serves for the preparation of Safranine T.

Alkyl Derivatives of *o*-Toluidine.—*o*-Toluidine is not so easily alkylated as aniline, presumably because of the presence of the methyl group in the *o*-position to the amino group. Thus it is possible to alkylate so that the main products are the secondary bases, and, on the other hand, alkylation to the tertiary bases is difficult. The tertiary bases derived from *o*-toluidine are not used as dyestuff intermediates, but the secondary bases have attained considerable importance, much more, in fact, than the secondary bases derived from aniline. Aniline supplies the tertiary bases required, while *o*-toluidine supplies the secondary bases. It is a matter of relative ease of preparation, and therefore of relative costs.

Methyl-*o*-toluidine—

$$\text{CH}_3$$
$$\text{NHCH}_3$$
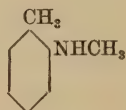
—a colourless liquid, b.p. 207° to 208°, D^{15} 0·973.

Acetyl derivative, m.p. 55° to 56°.

Ethyl-*o*-toluidine—

$$\text{CH}_3$$
$$\text{NHC}_2\text{H}_5$$
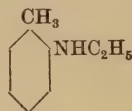
—a yellowish liquid, b.p. 214° to 216°, D^{15} 0·9534.

Acetyl derivative, b.p. 254° to 256°.

These two substances can be prepared, like the alkylanilines, by heating *o*-toluidine with the respective alcohols and a mineral acid at a somewhat higher temperature than that used for the alkylanilines. No precise details of the methods have been published. Monnet, Reverdin, and Noelting (*Ber.*, 1878, **11**, 2278) heated a mixture of 750 gms. of *o*-toluidine, 400 gms. of methyl alcohol, and 700 gms. of hydrochloric acid at 200° to 220° for a day. Probably sulphuric acid could be used in place of hydrochloric with advantage.

In the preparation of ethyl-*o*-toluidine, according to Thomas (*J.C.S.*, 1917, **111**, 562), and Price (*J.S.C.I.*, 1918, **37**, 82T), sulphuric acid can be used along with ethyl alcohol, although this has not been found possible in the ethylation of aniline. These authors give no details of their methods of preparation, but describe methods of removing unchanged *o*-toluidine from the secondary base. The former employs oxalic ester, which forms an oxamic ester with the toluidine, but does not react with the secondary base. The latter adds to the mixture sufficient 96 per cent. sulphuric

acid to form the sulphate of o-toluidine, which is insoluble in the remaining secondary base, and is removed by centrifuging and washing the sulphate with benzene or alcohol.

Of the two bases, ethyl-o-toluidine is the more widely used, presumably because it can be obtained in better yield than the methyl compound. They are used directly in making dyes of the triphenylmethane series, by condensation with chloro- and hydroxybenzaldehydes. These dyes are of various shades of blue, and are remarkably brilliant.

Indirectly, both bases are used also in preparing azine and thiazine colours, for which purpose their p-nitroso derivatives are prepared.

p-Nitrosoethyl-o-toluidine :

$$\underset{\text{ON}}{\overset{\text{CH}_3}{\bigcirc}}\text{NHC}_2\text{H}_5$$
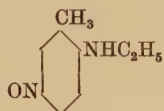
The base forms green leaflets (from benzene), m.p. 140°. Its hydrochloride forms yellow crystals soluble in water.

When nitrous acid acts on ethyl-o-toluidine, a nitrosamine is first formed, but this is transformed under the action of concentrated hydrochloric acid into the p-nitroso derivative :

$$\overset{\text{CH}_3}{\bigcirc}\text{NHC}_2\text{H}_5 \longrightarrow \overset{\text{CH}_3}{\bigcirc}\text{N(NO)C}_2\text{H}_5 \longrightarrow \underset{\text{ON}}{\overset{\text{CH}_3}{\bigcirc}}\text{NHC}_2\text{H}_5$$
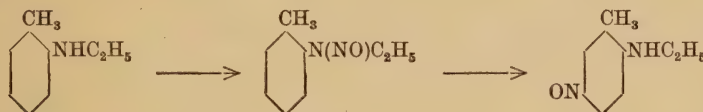
The method used by Fischer and Hepp (*Ber.*, **19,** 2994), who originally prepared such bodies for carrying out the transformation, was to isolate the nitrosamine by extraction with ether, add absolute alcohol to the ethereal solution, and saturate with gaseous hydrochloric acid. It has been found, however, that in the case of ethyl-o-toluidine the transformation proceeds partly in aqueous hydrochloric acid solutions of moderate strength, and can be made to go almost completely if the concentration of the hydrochloric acid is maintained at the maximum.

The preparation is described in G.P. 264927 as follows : 135 parts of ethyl-o-toluidine are dissolved in 400 parts of hydrochloric acid (20° Bé or 32 per cent.), the solution cooled to 0°, and a concentrated solution of 73 parts of sodium nitrite run in slowly, the temperature being kept about 0°. The nitrosamine separates as a yellow oil. This is extracted with ether or benzene, the solution dried, and the solvent evaporated off. It is then transformed by Fischer and Hepp's method. 500 parts of absolute alcohol are added to it, and the solution saturated in the cold with gaseous hydrochloric acid. After standing for some hours, the yellow hydrochloride of the p-nitroso compound crystallises out.

As mentioned above, this treatment with absolute alcohol may be omitted, with little sacrifice in yield, by using a more concentrated hydrochloric acid and keeping the water used in dissolving the nitrite to the minimum.

p-Nitrosomethyl-o-toluidine can be prepared in a similar manner.

These nitroso compounds are applied, like the nitroso derivatives of dimethyl- and diethylaniline (p. 51) in making dyes of the azine series (the Brilliant Rhodulines, etc.), and of the thiazine series (New Methylene Blue N).

o-**Chlorotoluene :**

CH₃
Cl

o-Toluidine can be converted, through its diazo compound, by means of the Sand-meyer reaction, into *o*-chlorotoluene. This forms a good alternative method to the more usual one (p. 127), as the yield obtained is high. The following is the procedure described by Ullmann ('' Organisches Chemisches Praktikum,'' p. 190) : 50 gms. of cupric chloride is dissolved in 100 c.c. of 33 per cent. hydrochloric acid and 20 c.c. of water. 20 gms. of zinc foil strips are added, and the mixture heated to boiling until the solution, at first dark brown, becomes pale brown, and the cuprous chloride begins to separate as a crystalline film on the surface.

While the cuprous chloride solution is cooling, 130 c.c. of 33 per cent. hydrochloric acid is stirred into 600 gms. of ice, the temperature of the mixture falling to − 18°. To this is added 54 gms. of *o*-toluidine, which dissolves and then separates as hydro-chloride. A solution of 35·5 gms. of sodium nitrite in 100 c.c. of water is now added quickly, with vigorous stirring. The temperature does not rise above 0°, no nitrous acid escapes, and starch-potassium-iodide paper should be faintly coloured blue by the solution. The diazo compound is then poured moderately quickly into the now almost decolourised cuprous chloride solution, keeping the temperature between 30° and 40°. Nitrogen is evolved, and the chlorotoluene separates as a brown oil. When the reaction is finished, the *o*-chlorotoluene is distilled off with steam. The distillate is shaken with caustic soda to dissolve out any *o*-cresol present. The chlorotoluene is then separated, warmed for a little with calcium chloride to dry it, and distilled. The yield of crude substance is 58 gms., and of the distilled, 53 gms., distilling between 152° and 160° (mostly at 156°). This corresponds to a yield of 85 per cent.

o-**Tolidine**—

H₃C   CH₃
H₂N   —   NH₂

—lustrous leaflets (from alcohol), m.p. 129°, easily soluble in alcohol and ether, sparingly soluble in water. 1 part dissolves in 1,000 parts of cold water or in 300 parts of boiling water.

It forms a **dihydrochloride,** of which 1 part dissolves in 17 parts of water at 12°, and also a more sparingly soluble monohydrochloride.

The **sulphate,** $C_{14}H_{16}N_2.H_2SO_4$, crystallises in needles or leaflets. 100 c.c. of water dissolve 0·12 gm. of the sulphate.

The **diacetyl** derivative melts at 315°.

o-Tolidine is prepared from *o*-nitrotoluene in the same way as benzidine from nitrobenzene—*i.e.*, by reduction of nitrotoluene to hydrazotoluene and transformation

of this by hydrochloric acid (p. 29).   The yield obtained is lower than that of benzidine, being about 64 to 65 per cent., using the process described by Schultz (see under Benzidine).   In this case, as in the case of benzidine, the hydrazo compound transforms partly to the o-p-diamino compound, and some fission also takes place with formation of o-toluidine.

o-Tolidine is used in making azo dyes of the same types as those derived from benzidine.   The shades produced are somewhat bluer than those of the corresponding benzidine dyes.

o-Tolidinedisulphonic acid :

$$H_3C \quad\quad CH_3$$
$$H_2N \underset{HO_3S}{\bigcirc} - \underset{SO_3H}{\bigcirc} NH_2$$

This is prepared like the corresponding benzidinedisulphonic acid (p. 33).

It forms a disodium salt ($+5H_2O$), which is readily soluble in hot water.

By coupling its tetrazo compound with β-naphthol a fast red wool dye, Milling Scarlet 5B or Acid Anthracene Red, is obtained.

5-Nitro-2-aminotoluene—

$$CH_3$$
$$\underset{O_2N}{\bigcirc} NH_2$$
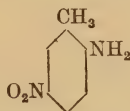
—crystallises from water in yellow needles, m.p. 127° to 128°.   It is sparingly soluble in boiling water, but easily soluble in alcohol.   It forms no salts.

This substance may be prepared, like p-nitroaniline, by nitration of the acetyl derivative of o-toluidine, but considerable quantities of the 3-nitro derivative are formed at the same time.   The 5-nitro compound is almost the sole product when the p-toluene-sulphonyl derivative of o-toluidine is nitrated (G.P. 157859, 163516, 164130, A.G.F.A.).

26·1 kg. of the p-toluenesulphonyl derivative of o-toluidine, in a finely powdered condition, is stirred into a mixture of 200 litres of water and 42 kg. of nitric acid (22·5° Bé).   The mixture is warmed on the water-bath, and nitration proceeds with alteration of the white crystals of the toluidide to yellow flocks of its 5-nitro derivative. About six to eight hours are required to complete the nitration.   The product is then filtered off, washed, and dried.   After recrystallising from alcohol it melts at 173° to 175°.   The toluenesulphonyl group is split off by warming the product with concentrated sulphuric acid, and the 5-nitro-2-aminotoluene isolated in the usual way.

B. Derivatives of p-Nitrotoluene.

p-Toluidine—

$$CH_3$$
$$\bigcirc$$
$$NH_2$$

—crystallises in leaflets (from dilute alcohol), m.p. 45°, b.p. 200·4° (760 mm.), D 1·058. It dissolves in 285 parts of water at 11·5°, and is easily soluble in alcohol, ether, and

benzene.   It is volatile in steam, 33 gms. distilling with 1 kg. of steam.   From the steam distillate it separates as a monohydrate in leaflets, m.p. 41·5°, which effloresce in air.

The **hydrochloride** forms leaflets or needles, m.p. 243°, soluble in water.

The **sulphate,** $(C_7H_9N)_2.H_2SO_4$, forms scales of which 5·06 parts dissolve in 100 parts of water at 22°.

The **acetyl** derivative crystallises from benzene in needles, m.p. 153°.

p-Toluidine is prepared by reduction of *p*-nitrotoluene in the usual way (p. 26).

It is used as a first component in a few monoazo dyes.   In conjunction with aniline it is employed in the manufacture of Magenta, the *p*-toluidine furnishing the " methane carbon " for the triphenylmethane molecule.   It is also largely applied in the preparation of acid wool colours of the anthraquinone series.   Hydroxyanthraquinones, especially those containing hydroxyl groups in α-positions, are condensed with *p*-toluidine so as to substitute the toluidino group for hydroxyl—*e.g.*:
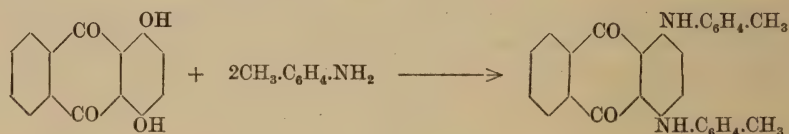
The products so formed are then sulphonated, the sulpho groups entering the tolyl nuclei.   *p*-Toluidine seems to be preferred to aniline for this purpose, probably because on sulphonation the sulpho groups take positions ortho to the —NH— groups, whereas in the case of aniline sulphonation would occur in the para positions.

p-**Nitrotoluene**-*o*-**sulphonic acid** :
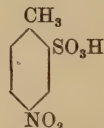
The acid crystallises from water in pale yellow prisms ($+2H_2O$), m.p. 133·5°.   From dilute sulphuric acid it crystallises water-free.   The anhydrous acid melts at 130°. 100 parts of water at 23° dissolve 67·7 parts of the acid.   It is also soluble in alcohol, ether, and chloroform.   The sodium salt is sparingly soluble in water.

This substance is obtained by sulphonating *p*-nitrotoluene with three times its weight of 25 per cent. oleum.   The mixture is stirred at a moderate temperature (25° to 30° will suffice, but the sulphonation is quicker at water-bath temperature), until a sample is soluble in water.   The solution is then poured into about three times its weight of saturated salt solution, when the sodium salt of *p*-nitrotoluenesulphonic acid separates almost quantitatively.   It is filtered off and pressed.   The product thus obtained may be used direct, or it may be purified by dissolving in hot water and salting out again.

p-Nitrotoluene-*o*-sulphonic acid undergoes a remarkable reaction when heated with caustic soda solution.   Simultaneous oxidation of the methyl group and reduction of the nitro group take place with formation of deeply coloured stilbene deriva-

tives. The first product is a blood-red solution, consisting chiefly of a dinitroso-stilbenedisulphonic acid :

$$\text{CH}=\!=\!=\text{CH}$$
$$\text{HO}_3\text{S}\bigcirc\quad\bigcirc\text{SO}_3\text{H}$$
$$\text{NO}\qquad\text{NO}$$
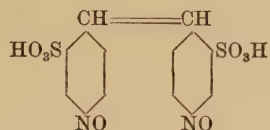
Continued action of alkali causes further condensation to form mixtures of yellow or orange dyestuffs, whose composition depends on the concentration of the alkali, on the temperature, and on the duration of heating. Dyestuffs of this kind are made by such empirical methods, and form the Stilbene Yellows and Mikado Yellows of commerce. They are direct cotton colours, and also dye wool and silk.

Dinitrostilbenedisulphonic acid :

$$\text{CH}=\!=\!=\text{CH}$$
$$\text{HO}_3\text{S}\bigcirc\quad\bigcirc\text{SO}_3\text{H}$$
$$\text{NO}_2\qquad\text{NO}_2$$
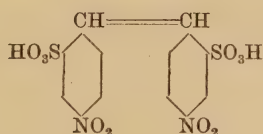
The acid crystallises in colourless or faintly yellow needles, soluble in water. The sodium salt is only moderately soluble in cold but easily in hot water. It is scarcely soluble in water containing caustic soda or sodium chloride.

This is prepared by oxidising p-nitrotoluenesulphonic acid in caustic alkaline solution with sodium hypochlorite.

Dinitrodibenzyldisulphonic acid—

$$\text{CH}_2\!-\!-\!-\!\text{CH}_2$$
$$\text{HO}_3\text{S}\bigcirc\quad\bigcirc\text{SO}_3\text{H}$$
$$\text{NO}_2\qquad\text{NO}_2$$
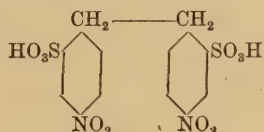
—is formed as an intermediate stage, and it is necessary, if the stilbene compound is to be used in making Chrysophenine, to ensure that the dibenzyl compound is completely oxidised to the stilbene. According to Green and Wahl (*Ber.*, **30,** 3078), the dibenzyl compound is favoured by a comparatively low temperature of oxidation, and by using a large excess of caustic soda, which precipitates the sodium salt of the dibenzyl compound as it is formed. On the other hand, the conditions favouring the stilbene compound are : less caustic soda, a higher temperature, and an excess of hypochlorite over the calculated amount. However, the temperature to be used is limited by the consideration that, as previously explained, p-nitrotoluene-o-sulphonic acid is readily converted in hot caustic alkaline solution into complex yellow and orange stilbene dyes. Green and Wahl (*loc. cit.*) oxidise at 50°, and also recommend this temperature in their English Patent, E.P. 5351 of 1897, but in their German Patent, G.P. 113514, the oxidation is performed at 80°.

The process described in the paper cited is as follows : To a solution of 100 gms. of sodium p-nitrotoluenesulphonate in 2 litres of warm water 200 c.c. of 30 per cent.

caustic soda and 500 c.c. of sodium hypochlorite solution (7 per cent. active chlorine) are added.   The mixture is warmed at 50° until the hypochlorite has almost disappeared.   On cooling, the sodium salt of dinitrostilbenedisulphonic acid crystallises out.

According to G.P. 113514, 200 gms. of p-nitrotoluenesulphonate is dissolved in 2 litres of water at 80° and, while stirring vigorously, 100 c.c. of 30 per cent. caustic soda is run in.   This is immediately followed by the addition of 234 c.c. of sodium hypochlorite solution (14 per cent. active chlorine) until a slight excess of unused chlorine is present.   Hydrochloric acid is then added until the solution is only faintly alkaline and the dinitrostilbenesulphonate is salted out.

Essentially the same process is described in G.P. 106961 (Levinstein), the only difference being that the caustic soda and hypochlorite solutions are mixed before adding.

The strength of the product in stilbene compound may be estimated by titration in ice-cold alkaline solution with standard permanganate.   The dibenzyl compound is not oxidised by permanganate under these conditions.

A number of yellow direct cotton colours of the same nature as those obtained from p-nitrotoluenesulphonic acid (p. 111) are derived from dinitrostilbenedisulphonic acid by heating with caustic soda solutions of various strengths at different temperatures.   Deeper shades are obtained by adding a reducing agent, such as glycerol, dextrose, or zinc dust.   Another series of dyes is obtained by condensing various primary amines, diamines, and aminophenols with dinitrostilbenedisulphonic acid in boiling caustic alkaline solution.   Unitary products are not obtained, and little is known of their constitution.   The processes used are purely empirical.   For the preparation of these dyes, the presence of dinitrodibenzyldisulphonic acid in the stilbene compound matters little, as it yields similar dyes.

Diaminostilbenedisulphonic acid :
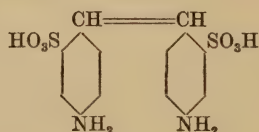
The acid forms a brownish-yellow crystalline powder, almost insoluble in water. The salts are easily soluble.

This was formerly prepared (G.P. 38735, Leonhardt and Co.) by boiling sodium p-nitrotoluenesulphonate with caustic soda solution until it was converted as far as possible into the dinitrosostilbenedisulphonic acid or Stilbene dyes previously mentioned (p. 111), and then reducing the product directly with zinc dust.   The yields obtained were not good.

Green and Wahl (E.P. 5351 of 1897) reduced dinitrostilbenedisulphonic acid with zinc dust, but, according to Fierz-David ("Farbenchemie," 1920, p. 119), the ordinary reduction method with iron can be used.   100 gms. of the crude sodium salt of dinitrostilbenedisulphonic acid is dissolved in 300 c.c. of hot water, neutralising at the same time any free alkali by a little dilute hydrochloric acid.   This solution is added during

half an hour to a boiling mixture of 200 gms. of iron borings, 20 c.c. of 40 per cent. acetic acid, and some water. After completion of the reduction and precipitation of dissolved iron by addition of the necessary sodium carbonate, the filtered solution is made strongly acid with hydrochloric acid, when diaminostilbenedisulphonic acid is precipitated, and after standing for ten hours is filtered off.

Diaminostilbenedisulphonic acid yields a tetrazo compound, and is used in making disazo dyes, of which that obtained by coupling with phenol and ethylating the product, named Chrysophenine, is the most important.

Dehydrothiotoluidine—
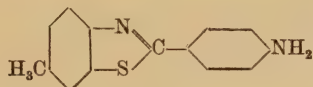
—crystallises from alcohol in brilliantly iridescent pale yellow prisms, m.p. 194·8°, b.p. 434° (766 mm.). It is almost insoluble even in boiling water, but is soluble in acetic acid, and moderately soluble in benzene, ether, and hot ethyl and amyl alcohols. The solutions generally show a violet-blue fluorescence.

It dissolves in concentrated hydrochloric acid to form an orange **dihydrochloride.** On adding water to the solution a yellow **monohydrochloride** precipitates.

The **acetyl** derivative melts at 227°.

It forms a yellow soluble **diazo** compound which shows great stability.

Dehydrothiotoluidine should be handled with care, as it gives rise, with most people, to an eczematic irritation of the skin.

Dehydrothiotoluidine forms part of the product obtained by heating p-toluidine with sulphur at 180° to 270°. The reaction was first studied by A. G. Green (see the article on " Primuline and its Derivatives " in Thorpe's " Dictionary of Applied Chemistry "), who showed that, as far as the formation of dehydrothiotoluidine was concerned, it occurred in accordance with the equation :

$$2C_7H_7.NH_2 \; + \; 4S \; = \; C_{14}H_{12}N_2S \; + \; 3H_2S$$
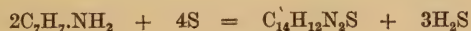
However, if p-toluidine and sulphur, in the proportion of 2 molecules of the former to 4 atoms of the latter, are heated until evolution of hydrogen sulphide ceases, further reactions take place and bodies of similar type but higher molecular weight are formed by a repetition of the first reaction with dehydrothiotoluidine itself. Thus there are formed a dithio and a trithio base, which have probably the constitutions :
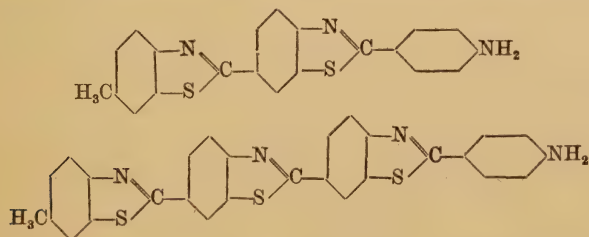
These latter bodies constitute that part of the product which is known as Primuline base. Besides these main products, there are found in the melt

8

small quantities of the *o*-thiophenol derivative of *p*-toluidine (I) and thio-*p*-toluidine (II) :
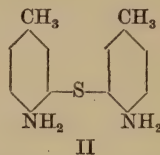
Some *p*-toluidine is always left unchanged.   Apart from these by-products, the product obtained by heating 2 molecules of *p*-toluidine with 4 atoms of sulphur contains about 50 per cent. of dehydrothiotoluidine and 40 per cent. of primuline base.   The proportion of dehydrothiotoluidine to primuline in the melt can be raised by lowering the proportion of sulphur to *p*-toluidine, but no conditions have been found to yield dehydrothiotoluidine without some accompanying primuline base.   Green (*loc. cit.*) recommends the proportion of 2 atoms of sulphur to 2 molecules of *p*-toluidine if dehydrothiotoluidine is required.   The preparation in that case would be carried out as follows :

214 parts of *p*-toluidine and 64 parts of sulphur are heated together in a vessel provided with an air condenser and some means of absorbing the hydrogen sulphide evolved later.   The temperature is slowly raised, and at 170° to 180° hydrogen sulphide is given off.   The heating is regulated so that the reaction does not become too violent.   When the evolution of gas slackens, the temperature is slowly raised to about 210° and maintained at this point until no more hydrogen sulphide is given off. The unchanged *p*-toluidine is then distilled off under reduced pressure, this being followed by small quantities of the above-mentioned by-products.   The residual liquid is chiefly dehydrothiotoluidine, but contains some primuline and other impurities.   It can be used directly by running the melt on to iron plates and powdering the solid cakes when cold.   If pure dehydrothiotoluidine is required, the only satisfactory method of obtaining it is to continue the vacuum distillation at a sufficiently high temperature to drive over the dehydrothiotoluidine itself.   Recrystallisation of the crude melt from solvents is useless.

G.P. 53938 (Cassella) recommends the addition of naphthalene to the melt in order to prevent the temperature from rising above 210°, but this is unnecessary if the above proportions are used, since the excess of *p*-toluidine serves the same purpose and is more easily removed from the finished melt.

Dehydrothiotoluidine is used as a first component in azo dyes, α-naphtholsulphonic acids being generally used as end components.   These dyes, like those obtained from benzidine, are direct cotton colours.   They also possess affinity for wool and silk, and are therefore used in dyeing union materials.

A basic dye, Thioflavine T, is also made from dehydrothiotoluidine by methylation of the base so far as to form a monoquaternary ammonium salt :

Dehydrothiotoluidinesulphonic acid :

$$\text{H}_3\text{C} \underset{S}{\overset{N}{\diagdown}} \text{C.C}_6\text{H}_3(\text{SO}_3\text{H}).\text{NH}_2$$
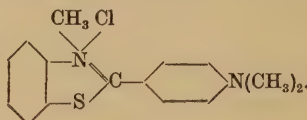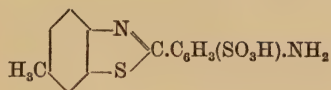
The acid forms small yellow needles (with $1\text{H}_2\text{O}$) or orange leaflets (with $2\text{H}_2\text{O}$). It is insoluble in cold and sparingly soluble in hot water. The salts are colourless, and mostly moderately soluble in water, the solutions showing a violet-blue fluorescence. The ammonium salt crystallises in fine white needles ($+\text{H}_2\text{O}$), and is sparingly soluble. The acid yields a yellow sparingly soluble diazo compound, which is stable even in boiling water.

The sulphonic acid just described is prepared by the sulphonation of dehydrothiotoluidine with oleum containing a high percentage of free sulphur trioxide. The exact position of the sulpho group is unknown.

The published descriptions of the preparation of this acid ("Primuline," etc., by A. G. Green, Thorpe's "Dictionary of Applied Chemistry"; Jansen, *Zeit. Farbenind.* 1913, **12**, 215) deal with the sulphonation of the so-called primuline melt, which is obtained by heating *p*-toluidine and sulphur in the proportion of 2 molecules of the former to $4\frac{1}{2}$ atoms of the latter. The melt so obtained contains about 60 per cent. of primuline base, and only 30 to 35 per cent. of dehydrothiotoluidine. It yields a mixture of the sulphonic acids of both bases, from which dehydrothiotoluidine-sulphonic acid is separated by means of its sparingly soluble ammonium salt.

Formerly, it was the primuline which was chiefly desired, but in recent years the use of dehydrothiotoluidine and its sulphonic acid has greatly extended, while that of primuline has declined. The primuline melt has, therefore, probably been modified by reduction of the proportion of sulphur used so as to yield a larger percentage of dehydrothiotoluidine. However, the sulphonation process is essentially the same, whatever the proportions of the bases in it, and the following summary of the process described by Green is applicable to any modified melt or even to the high percentage crude dehydrothiotoluidine previously described.

The melt is carried out by heating a mixture of 1,000 lbs. of *p*-toluidine and 670 lbs. of sulphur in an enamelled iron pot provided with an enamelled stirrer and an air condenser. The mixture is boiled for several hours, during which hydrogen sulphide is evolved and the temperature gradually rises. The evolution of hydrogen sulphide begins at 170°, and is completed when the temperature reaches 270°. The melt is then discharged from the pot, cooled, and powdered when solid. The yield is about 1,125 lbs.

400 lbs. of the powdered melt is dissolved with rapid stirring in 1,000 lbs. of 100 per cent. sulphuric acid. The temperature is allowed to rise freely during this operation, and reaches about 90°. The solution is then cooled below 40°, and 800 to 900 lbs. of 70 per cent. oleum slowly added, the temperature being kept about 40°. About six hours are required for the addition. Stirring is then continued until sulphonation is complete, as shown by the sulphonic acids, precipitated from a sample by dilution with water, dissolving to a perfectly clear solution in boiling dilute ammonia. It

is necessary to make sure that this test is complied with, otherwise difficulty arises later in filtering the precipitated sulphonic acids. On the other hand, the course of the sulphonation must be followed closely by means of this test so as to determine exactly the point of completed sulphonation. If the reaction is continued beyond this point soluble disulphonic acids are formed, resulting in diminished yield, especially of dehydrothiotoluidinesulphonic acid.

When sulphonation is complete, the solution is run into about 3,000 gallons of cold water, and the sulphonic acids, which separate as a bulky orange-yellow precipitate, are filtered off and washed completely free of mineral acid with cold water. The paste of mixed sulphonic acids is then stirred into cold concentrated ammonia, sufficient being used to give a slight excess of free ammonia. Both acids dissolve up as ammonium salts, but that of the dehydrothiotoluidinesulphonic acid soon begins to crystallise out, and after standing for a few days to complete the separation, is filtered off and washed with a little cold water.

The filtrate, which contains the soluble ammonium salt of primuline, is treated with common salt, when the primuline is salted out as a dark yellow granular precipitate.

The yields obtained are 530 to 560 lbs. of ammonium dehydrothiotoluidinesulphonate and 1,700 to 1,800 lbs. of primuline of standard dyeing strength from 1,000 lbs. of p-toluidine.

In G.P. 281048 (Bayer) is described the preparation of a dehydrothiotoluidinesulphonic acid, which is said to be different from that mentioned above. The bake process is used, and the product is, therefore, probably the o-sulphonic acid :
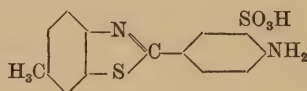
240 parts of dehydrothiotoluidine are intimately mixed with a solution of 147 parts of 100 per cent. sulphuric acid in water, and the mixture is heated till dry. It is then finely powdered and heated *in vacuo* at 235° to 250° in a vessel provided with a stirrer and an air condenser. When no more water distils over, the sulphonic acid is dissolved up in hot water and the necessary alkali, the solution filtered, and on cooling the sodium salt crystallises out as colourless leaflets. This sulphonic acid also yields a yellow sparingly soluble diazo compound. It is said to yield azo dyes of greater intensity and better light fastness than those obtained from the sulphonic acid prepared in the ordinary way.

Dehydrothiotoluidinesulphonic acid is used as a first component in several monoazo dyes which, like those obtained from dehydrothiotoluidine base, are direct cotton colours. With α- and β-naphtholsulphonic acids as second components, the dyestuffs obtained give pink and scarlet shades on cotton. Dyestuffs, which are probably of the azo class, are also obtained by condensing dehydrothiotoluidinesulphonic acid with dinitrostilbenedisulphonic acid in alkaline solution.

By coupling diazotised dehydrothiotoluidinesulphonic acid with a molecular proportion of the acid itself, a diazoamino compound is obtained, known as Thiazole

Yellow, which gives very intense but very fugitive shades on cotton. On the other hand, by oxidising dehydrothiotoluidinesulphonic acid with sodium hypochlorite an exceedingly fast yellow dyestuff is obtained.

Primuline is often used in place of dehydrothiotoluidinesulphonic acid, and yields dyes of almost identical shades and similar properties.

3-**Nitro**-4-**aminotoluene** (*m*-**nitro**-*p*-**toluidine**) :

$$CH_3$$
$$NO_2$$
$$NH_2$$
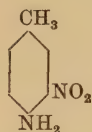
The base forms red prisms, m.p. 117° to 118°, soluble in alcohol. Its **acetyl** derivative crystallises in lemon-yellow needles, m.p. 94° to 95°.

This substance is prepared by nitration of the acetyl derivative of *p*-toluidine, either in sulphuric acid solution, as in the preparation of *p*-nitroaniline, or in solution in glacial acetic acid (Ehrlich, *Ber.*, **15,** 2009). The nitro-*p*-acetotoluidine so produced is then hydrolysed by boiling with concentrated hydrochloric acid or with caustic alkali.

This nitrotoluidine, by coupling its diazo compound with β-naphthol, forms a bright red lake pigment of excellent quality as regards fastness to water, lime, and heat. It is also used in conjunction with Naphthol AS for producing red dyeings on cotton.

C. **Derivatives of** 2 : 4-**Dinitrotoluene.**

m-**Tolylenediamine**—

$$CH_3$$
$$NH_2$$
$$NH_2$$
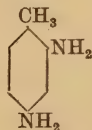
—crystallises in prisms or needles (from water), m.p. 99°, b.p. 283° to 285°. It is easily soluble in boiling water, but much less so in cold water. The diacetyl derivative melts at 224°.

It is prepared from 2 : 4-dinitrotoluene in the same way as *m*-phenylenediamine from *m*-dinitrobenzene.

m-Tolylenediamine resembles *m*-phenylenediamine closely in properties and in chemical behaviour. By the action of nitrous acid it gives a Bismarck Brown of redder shade than that formed from *m*-phenylenediamine. It is used as an end component in various mono-, dis-, and trisazo dyes.

Acridine dyes are formed from it by condensation with formaldehyde and benzaldehyde.

It is also used in the preparation of several sulphur colours by heating it with sodium polysulphides under various conditions.

m-**Tolylenediaminesulphonic acid** :

$$\text{HO}_3\text{S}\underset{\text{NH}_2}{\overset{\text{CH}_3}{\bigcirc}}\text{NH}_2$$
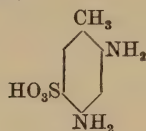
The acid crystallises in small prisms, sparingly soluble in water.   The sodium salt crystallises with $4\text{H}_2\text{O}$, and is soluble in water.

It is prepared by adding *m*-tolylenediamine sulphate gradually to the calculated quantity of oleum and heating the solution for about three hours on the water-bath. When the sulphonation is finished, the solution is poured on ice, and the sulphate of the sulphonic acid separates.   This is converted to the hydrochloride, and used direct for azo dyes (Bückel, *Zeit. Farbenind.*, 1904, **3**, 137).

4-Nitro-2-aminotoluene—

$$\underset{\text{NO}_2}{\overset{\text{CH}_3}{\bigcirc}}\text{NH}_2$$
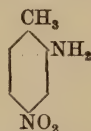
—crystallises from alcohol as large orange-yellow prisms with blue reflex, m.p. 107°, b.p. 310°.   It dissolves in 100 parts of boiling water.

This compound can be prepared, either by reducing 2 : 4-dinitrotoluene or by nitrating *o*-toluidine by Noelting and Collin's method, in which the base is nitrated in a large excess of concentrated sulphuric acid.

The former method seems preferable as giving a product free from isomers. Reduction with ammonium sulphide or sodium disulphide does not give good results in this case, but, according to G.P. 289454 (Pomeranz), reduction with iron and sulphur dioxide, which is equivalent generally to reduction with alkaline sulphides, is specially suitable.

A mixture of 182 gms. of 2 : 4-dinitrotoluene, 200 gms. of iron borings, and 1 litre of water, is warmed to 80° to 90°, and excess of sulphur dioxide passed in.   The iron dissolves except for a small residue, which is filtered off, and on cooling the nitro-toluidine crystallises out.   The yield obtained is 110 gms. or about 80 per cent.

On nitrating *o*-toluidine dissolved in a large excess of sulphuric acid the product contains 75 per cent. of 4-nitro-2-aminotoluene, about 20 per cent. of 6-nitro compound (m.p. 91·5°) and 3 to 4 per cent. of the 5-nitro compound (m.p. 130°).   The large scale preparation of the 4-nitro compound by this method is described by Jansen (*Zeit. Farbenind.*, 1913, **12**, 181).

192 kg. of *o*-toluidine is added very slowly, with good stirring and cooling arrangements, to 840 kg. of 98 per cent. sulphuric acid, the temperature being allowed to rise to 30° to 35°.   White lumps of the sulphate form on the surface of the acid, but these redissolve.   The solution is then cooled to 10° and a mixture of 125 kg. of 90 per cent. nitric acid and 300 kg. of 98 per cent. sulphuric acid is dropped in through a funnel, whose end dips beneath the surface of the solution.   During the addition the temperature is kept at 10°, except towards the end, when it is allowed to rise to 12°.   When

the nitration is finished, the solution is run into 4,500 litres of a solution containing 1,200 kg. of salt.   The sulphate of 4-nitro-2-aminotoluene separates as a pale yellow crystalline mass, while the 6-nitro compound remains in solution.   After twenty-four hours' stirring, the precipitated sulphate is filtered and washed with small quantities of saturated salt solution.   The yield obtained is 190 kg., reckoned as base.

The diazo compound of 4-nitro-2-aminotoluene is coupled with β-naphthol to form an orange lake pigment.   It is also used with β-naphthol and Naphthol AS to produce orange and scarlet dyeings on cotton by a similar method to that used for Para Red.

CHAPTER VI

THE CHLORINATION AND SULPHONATION
OF TOLUENE

THE action of chlorine or chlorinating agents on toluene proceeds in two ways, according to conditions—viz., by substitution either in the nucleus or in the side chain. A third possibility—the formation of addition products—has apparently not been observed. At the boil, or in the cold in sunlight, side chain chlorination takes place, if catalysts are absent. In the presence of catalysts such as iodine and many metallic chlorides, nuclear chlorination occurs.

A comprehensive review of the literature on the chlorination of toluene is given by Cohen and Dakin (*J.C.S.*, 1901, **79**, 1111), who also give the results of further investigations in later papers (*J.C.S.*, 1905, **87**, 1034; 1910, **97**, 1623).

Benzyl chloride—

$$CH_2Cl$$
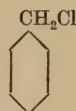
—a colourless liquid having a characteristic aromatic odour. The vapour is irritating to the eyes. B.p. 179°. D_{15}^{15} 1·104. It is insoluble in water, but is slowly hydrolysed by boiling with water, yielding benzyl alcohol, $C_6H_5.CH_2OH$.

The usual method of preparation of this substance is to pass dry chlorine into dry boiling toluene, to which about 2 per cent. of phosphorus trichloride or pentachloride has been added to accelerate the reaction, until the theoretical increase in weight is obtained. Iron vessels cannot be used, since iron induces nuclear chlorination, lead vessels being undesirable, though not absolutely prohibitive, for a similar reason.* Enamelled or tile-lined vessels have been used. In Germany, glass vessels heated in calcium chloride baths are sometimes employed. The reaction is also sometimes further accelerated by use of the light from a quartz-mercury lamp. Provision, of course, has to be made for absorbing the hydrochloric acid evolved.

When the chlorination has reached the desired stage, the product is washed with very dilute alkali and then fractionated. It contains, besides benzyl chloride, some unchanged toluene and the higher chlorination products, benzal chloride and benzotrichloride.

A continuous manufacturing process is described by Marckwald in G.P. 142939 (E.P. 17695 of 1902).

The use of nascent chlorine, by passing sulphur dioxide into a mixture of toluene and bleaching powder, was suggested by Conant (U.S.P. 1233986). A similar idea, carried out in an aqueous medium, is the subject of a patent by Levinstein and Bader (E.P. 134250). Toluene (3 mols.) is emulsified, by rapid stirring, with a sodium hypochlorite solution containing 1 molecule of active chlorine. The mixture is cooled to – 5° and dilute sulphuric acid ($\frac{1}{2}$ mol.) or other acid added gradually during

* Wahl, Normand, and Vermeylen (*C.r.*, 1922, **174**, 946), found that chlorination of toluene in presence of lead chloride gave a mixture consisting mainly of *o*- and *p*-chlorotoluenes.
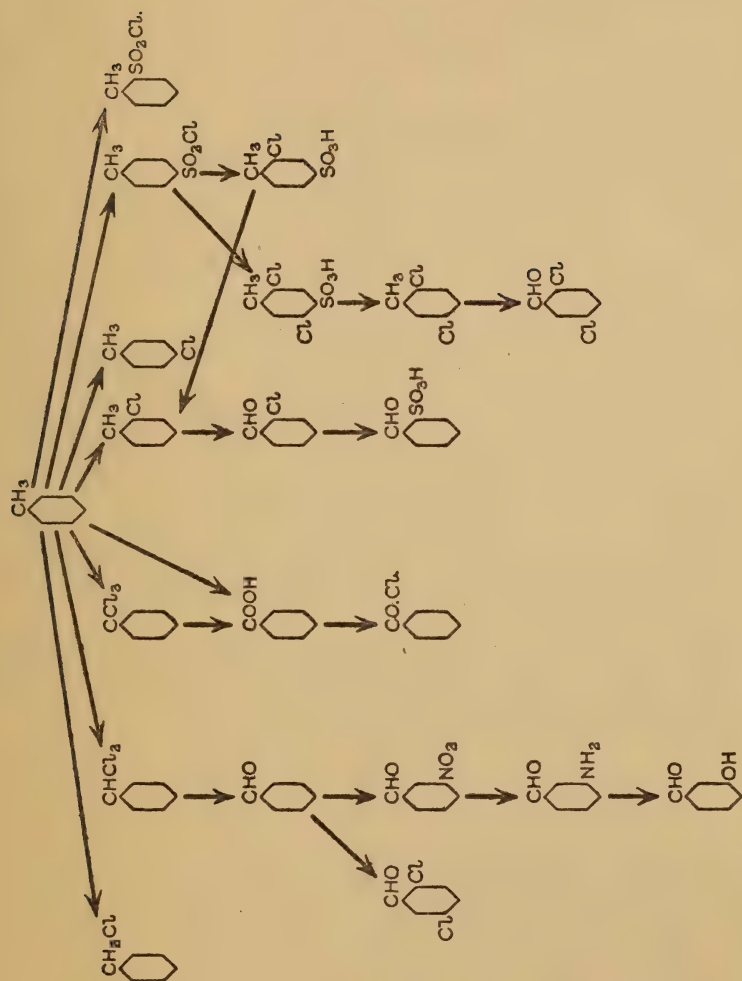
CHART VI.—DERIVATIVES OF TOLUENE BY CHLORINATION AND SULPHONATION.

six hours.   The mixture is then allowed to settle, and the chlorinated toluene layer separated.   On fractionation it gives unchanged toluene, benzyl chloride, and a small residue of benzal chloride, etc.   The yield of benzyl chloride is 60 to 70 per cent. calculated on the active chlorine used.

Benzyl chloride is used in benzylating amines, especially the secondary alkyl-anilines.

Benzal chloride—

—a strongly refracting liquid, b.p. 206°, D^{14} 1·2557.

Benzotrichloride—

—a strongly refracting liquid, b.p. 213° to 214°, D^{14} 1·380.

These two substances are usually prepared together in varying proportions by passing chlorine into toluene, as described in the case of benzyl chloride.   They cannot be separated by fractional distillation, but their respective products of hydrolysis, benzaldehyde, and benzoic acid, are easily separated.   The passage of the chlorine is, therefore, continued until the desired proportions of benzal chloride and benzotri-chloride are formed, as indicated by the increase in weight, or, more conveniently, by the specific gravity of the liquid.   The mixture, after removal of any unchanged toluene and benzyl chloride by fractional distillation, is then hydrolysed to benzalde-hyde and benzoic acid, as described later.

Complete chlorination to benzotrichloride is not usually attempted, partly because the last of the chlorine is only slowly taken up, and partly because the tendency towards nuclear chlorination greatly increases at this stage.

Benzaldehyde—

—a colourless highly refracting liquid of characteristic aromatic odour, b.p. 179·1° (751 mm.), 62° (10 mm.).   It freezes at − 13·5°. D^{15}_{4} 1·0504.   It dissolves in 300 parts of water.

Benzaldehyde is prepared either by hydrolysis of benzal chloride or by direct oxidation of toluene.   The hydrolysis of benzal chloride, which was formerly carried out by heating with milk of lime in autoclaves, is now accomplished, at ordinary pressure and at water-bath temperature, by water with the addition of a little iron powder as catalyst.   This improvement was introduced by Schultze (G.P. 82927, 85493).   The ordinary crude mixtures of benzal chloride and benzotrichloride are used, any benzyl chloride being previously removed by fractionation.   The

benzotrichloride undergoes a similar hydrolysis, with formation of benzoic acid.

In a lead-lined (or copper) vessel, 60 kg. of the crude benzal and benzotrichlorides is warmed to 25° to 30°, 20 gms. of iron powder added and, after fifteen to thirty minutes, 10 to 15 kg. of water. The mixture is warmed gradually to 90° to 95°, and the reaction, once started, proceeds vigorously. The hydrochloric acid evolved is absorbed in water. When the evolution of gas has ceased, the mixture is made alkaline with milk of lime made from 9 to 10 kg. of quicklime and the benzaldehyde distilled off with steam. The residual aqueous liquor is filtered, and the filtrate acidified, when benzoic acid is precipitated.

The benzaldehyde obtained from the steam distillate contains as impurities chlorotoluenes, benzyl alcohol, etc. It is purified through its bisulphite compound. The crude product is agitated with four to five times its weight of ordinary 35 per cent. bisulphite solution until the benzaldehyde is dissolved. After allowing to settle, the bisulphite compound is separated from the undissolved oily impurities. The solution is then made alkaline with soda and distilled with steam. The separated and dried benzaldehyde is finally purified by distillation.

Benzaldehyde is also prepared, as mentioned above, by direct oxidation of toluene. Manganese dioxide, in conjunction with sulphuric acid, has been found to be the best oxidising agent for this purpose, and the process is described in G.P. 101221 (*Société Chimique des Usines du Rhône*). 300 kg. of toluene and 700 kg. of 65 per cent. sulphuric acid are thoroughly mixed by rapid stirring, and 90 kg. of finely divided manganese dioxide (the regenerated oxide should be used) is gradually added, while the temperature is kept at 40°. When the reaction is ended, the benzaldehyde and unchanged toluene are distilled with steam, and the benzaldehyde separated from the toluene and purified by the bisulphite method. The yield of benzaldehyde is 50 kg. and 250 kg. of toluene is recovered. A little dibenzyl, $C_6H_5.CH_2.CH_2.C_6H_5$, is always formed as a by-product. The essential feature of the method is that, in order to avoid further oxidation to benzoic acid, a large fraction of the toluene is left unoxidised. According to a later patent by the same firm (G.P. 107722), however, the whole of the toluene may be oxidised to aldehyde without fear of this further oxidation.

An improvement in the purification process was introduced by the Griesheim-Elektron firm in G.P. 154499. The crude aldehyde is mixed with water and sulphur dioxide passed in at the ordinary temperature. A soluble compound of the aldehyde with sulphur dioxide is formed. After separating the solution from the undissolved matter, it is heated to 100°, when the compound decomposes, sulphur dioxide being evolved, and the benzaldehyde is separated from the water.

Benzaldehyde is used chiefly in the production of dyes of the triphenylmethane series by condensing it with two molecular proportions of a tertiary base derived from aniline, such as dimethylaniline, benzylethylaniline, etc., and oxidising the condensation product. The resulting dyes are basic and dye textiles in various shades of green.

Basic dyes of the acridine series are also made from benzaldehyde by condensing it with *meta*-diamines, such as *m*-tolylenediamine.

m-**Nitrobenzaldehyde**—

$$CHO$$
$$NO_2$$
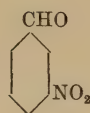
—pale yellow crystals, m.p. 58°, b.p. 164° (23 mm.).

This substance forms the main product when benzaldehyde is nitrated in the ordinary way with mixed acid (Friedländer and Henriques, *Ber.*, 1881, **14,** 2802). At low temperatures, about 5°, *o*-nitrobenzaldehyde is practically the only other product, but at temperatures above the ordinary the *p*-isomer is also formed to some extent.

The nitration is described in detail in U.S.P. 1509412. Mixed acid having the composition—

HNO_3	..	..	..	..	..	..	28-30 per cent.
H_2SO_4	..	..	..	..	..	..	63-66 ,,
H_2O	..	..	..	..	..	..	4-7 ,,

—is used. $7\frac{1}{2}$ litres of this acid is cooled below 15°, and 3 kg. of benzaldehyde added at such a rate that the temperature can be kept between 5° and 15°. About six hours are required for the addition. The mixture is stirred for an hour longer to complete the nitration. It is then poured into 18 kg. of ice and 43 kg. of water, stirred, and allowed to settle. The dilute acid layer is run off, and the oily mixture of aldehydes washed first with warm water and then with warm dilute soda solution until acid-free. The temperature of the washing liquors should be about 40° in order to keep the aldehydes liquid. The oil is then cooled to 10° and stirred until it has crystallised as far as possible. The crystals of *m*-nitrobenzaldehyde are separated from the remaining oil by centrifuging. This gives a fairly pure product.

The residual oil contains *o*-nitrobenzaldehyde (which forms about 20 per cent. of the total product) mixed with a little *m*-compound and some dinitrobenzaldehydes.

m-**Aminobenzaldehyde :**

$$CHO$$
$$NH_2$$
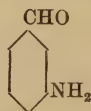
This is prepared by reduction of the bisulphite compound of *m*-nitrobenzaldehyde, since the nitrobenzaldehyde is not itself easily reduced. The reduction may be carried out by iron or zinc and acid, as in G.P. 62950 (Meister Lucius and Brüning), but better results are obtained by the process described in G.P. 66241 by the same firm.

680 kg. of ferrous sulphate crystals are dissolved in 2,000 litres of water and 250 kg. of precipitated chalk added. The mixture is boiled and vigorously stirred while a solution of 60 kg. of *m*-nitrobenzaldehyde in 120 kg. of 30 per cent. bisulphite and 500 litres of water is run in slowly. The reduction is immediate. Much frothing takes place owing to the carbon dioxide evolved. The mixture is filtered hot, and the filtrate, acidified with hydrochloric acid, is boiled to expel sulphur dioxide. The

resulting solution of *m*-aminobenzaldehyde hydrochloride is used direct, chiefly for the preparation of *m*-hydroxybenzaldehyde.

m-**Hydroxybenzaldehyde**—

CHO

OH
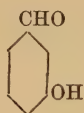
—m.p. 107°, b.p. 240°, or 160° to 161° (20 mm.).

This substance is prepared by diazotising *m*-aminobenzaldehyde and boiling the solution of diazo compound. No details of the method have been published.

m-Hydroxybenzaldehyde is used in making Cyanol FF, a triphenylmethane dye, by condensing the aldehyde with ethyl-*o*-toluidine and sulphonating the product, when two sulpho groups enter the aldehyde nucleus.

Benzoic acid—

COOH

—lustrous needles or leaflets, m.p. 121·4°, b.p. 249°, D_4^{15} 1·2659. It sublimes readily, and is volatile in steam. 100 parts of water at 10° dissolve 2 parts, and at 75° 22 parts of benzoic acid. It is also soluble in alcohol, ether, and chloroform. The sodium salt crystallises with $1H_2O$.

Benzoic acid is prepared either from benzotrichloride or directly from toluene by oxidation. The former process is the cheaper of the two, but yields a product containing chlorobenzoic acids and other chloro derivatives, while the latter gives a chlorine-free benzoic acid.

As explained in connection with the preparation of benzotrichloride, the chlorination of toluene is not carried so far as to convert the toluene completely to the trichloride owing to the increasing extent of nuclear chlorination towards the end. If benzoic acid is required as the chief product, chlorination is continued until the specific gravity of the liquid reaches 1·34 to 1·37 (S.G. of benzotrichloride : 1·39), and the resulting mixture of benzal chloride and benzotrichloride is hydrolysed by the process of G.P. 85493, as described under Benzaldehyde (p. 123). Benzoic acid in this case is the main product, with benzaldehyde as by-product.

Toluene can be oxidised to benzoic acid by manganese dioxide and sulphuric acid, but for good yields stronger oxidising agents are required. A process of oxidation with chromic acid is described in G.P. 261775 (Buckau). A solution containing 130 gms. of chromic acid and 300 to 400 gms. of sulphuric acid per litre is heated to 85° to 100°, and toluene vapour passed through. Benzoic acid is formed, and is dissolved up by the toluene layer, which accumulates on the surface of the chromic acid solution, thus being removed from further attack by the oxidant. The toluene-benzoic acid solution is separated from the acid layer and the benzoic acid isolated. The chromic sulphate is reoxidised electrolytically and used again. The yield of benzoic acid is 70 to 90 per cent. of the toluene consumed.

Benzoic acid is used in the preparation of a few chrome wool colours belonging to different chemical classes. It condenses with pyrogallol yielding a trihydroxybenzophenone, which constitutes the commercial dye Alizarine Yellow A. Condensed with gallic acid it forms a trihydroxyanthraquinone, a chrome brown (Anthracene Brown) of excellent fastness qualities :
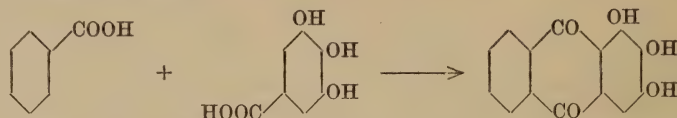
It also reacts with Michler's hydrol to form a triphenylmethane dye, Chrome Green, the condensation taking place in the *meta* position to the carboxyl group.

Benzoic acid is also used as a catalyst in the phenylation of Rosaniline to produce the Aniline Blues, its exact function being unexplained.

Benzoyl chloride, $C_6H_5.CO.Cl$, a colourless liquid, b.p. 198°, D_4^{20} 1·2122, may be prepared from benzoic acid by the action of phosphorus pentachloride, but some cheaper reagent is generally used.

G.P. 146690 proposes to use sodium chlorsulphonate, which is prepared by heating chlorsulphonic acid with the calculated quantity of sodium chloride at 150° until evolution of hydrochloric acid ceases. 170 parts of sodium chlorsulphonate and 150 parts of sodium benzoate (anhydrous) are heated together until the benzoyl chloride formed distils off :

$$C_6H_5.COONa + Cl.SO_3Na \longrightarrow C_6H_5.CO.Cl + Na_2SO_4$$
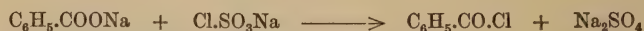
Thionyl chloride and sulphuryl chloride have also been used.

Benzoyl chloride is chiefly used in benzoylating aminoanthraquinones to produce vat dyes of the Algol series. The benzoyl derivatives are found to possess good affinity for cotton, a property which is almost entirely lacking in the free amino compounds.

The Chlorotoluenes.

The conditions favouring the substitution of chlorine in the nucleus of toluene are (1) low temperatures (ordinary temperature is suitable), and (2) the presence of catalysts. Iodine, as catalyst in this case, seems not merely to favour nuclear chlorination, but actually to hinder side-chain chlorination even at the boiling-point. Ferric chloride and molybdenum chloride are also useful as catalysts in this reaction. When toluene is chlorinated under these conditions, a mixture of *o*- and *p*-chlorotoluenes is formed, together with some dichloro derivatives. On fractionating the product a mixture of the two monochlorotoluenes can be isolated, but they cannot be separated from one another by distillation owing to the closeness of their boiling-points. A method of separation is described below. Of the two, only the *o*-compound has found much application in the dyestuff industry.

o-**Chlorotoluene—**
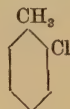
—a colourless oil, b.p. 159°, D_{15}^{15} 1·0877. It freezes at $-34°$. (*p*-**Chlorotoluene,** liquid, b.p. 162°, D_{15}^{15} 1·0749. Freezes at 7·4°.)

The two monochlorotoluenes may be separated, according to E.P. 159837 (Wahl), by a process which depends on the fact that *o*-chlorotoluene is more readily sulphonated than the *p*-compound, and that the conditions of sulphonation as regards temperature and acid concentration can be so arranged that only *o*-chlorotoluene is sulphonated.

The mixture of chlorotoluenes (40 parts) is heated with 75 parts of 93 per cent. sulphuric acid at 114° to 115° for two and a half hours. In this way nearly all the *o*-compound is sulphonated and the *p*-compound, together with the small residue of unsulphonated *o*-compound, remains as an oil which is separated from the acid layer on cooling. The solution of *o*-chlorotoluenesulphonic acid is then heated to 180° and superheated steam passed through. The sulphonic acid is hydrolysed, *o*-chlorotoluene distils with the steam and is separated from the distillate.

A better process, and one which avoids the formation of *p*-chlorotoluene, is that described in G.P. 294638 (Badische). Toluene-*p*-sulphonic acid is chlorinated, the chlorine entering the *o*-position only, and *o*-chlorotoluene is then easily obtained by hydrolysis of the sulphonic acid. The toluene-*p*-sulphonic acid is most conveniently obtained from its chloride (p. 130). The direct chlorination of toluene-*p*-sulphonyl chloride, however, is useless, as the chlorine partly expels the —SO_2Cl group.

300 parts of molten toluene-*p*-sulphonyl chloride is run slowly into 300 parts of sulphuric acid (60° Bé) at 95°. A vigorous evolution of hydrochloric acid takes place, and the liquid is further heated at 100° for two hours in order to expel the hydrochloric acid completely. The solution is cooled to 20° and 3 parts of sublimed ferric chloride added. Chlorine is then led in until the specific gravity of the solution, originally 49·5° Bé, rises to 53·5° Bé, when the formation of *o*-chlorotoluene-*p*-sulphonic acid is complete. This is now hydrolysed directly with superheated steam, as described above, and the separated *o*-chlorotoluene purified by distillation.

If toluene-*p*-sulphonyl chloride is not available, toluene may be sulphonated under the conditions specified by Hollemann (*Ber.*, 1911, **44**, 2508), so as to form the maximum proportion of the *p*-sulphonic acid. This idea is used in G.P. 287932 (Meister Lucius and Brüning), an alternative method of chlorination being also described.

Toluene (460 parts) is sulphonated by heating with 2,300 parts of 84 per cent. sulphuric acid at 100° to 105° for seven hours. The proportion of *p*-sulphonic acid formed is about 85 per cent. The solution is poured into 2,600 parts of ice, and after adding 600 parts of common salt and 900 parts of concentrated hydrochloric acid, chlorination is carried out by slowly adding during eight hours a solution of 250 parts of sodium chlorate, the temperature being kept at 55°. The sodium salt of *o*-chlorotoluene-*p*-sulphonic acid crystallises out and, after cooling and stirring for several hours, is filtered off. An 80 per cent. yield of pure sodium-*o*-chlorotoluene-*p*-sulphonate is thus obtained. The filtrate contains *p*-chlorotoluene-*o*-sulphonate. The *o*-chlorotoluene-*p*-sulphonate is then hydrolysed, as already described, to form *o*-chlorotoluene.

Another method of preparation of o-chlorotoluene—from o-toluidine—is described on p. 108.

o-**Chlorobenzaldehyde**—
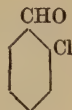
—a colourless liquid, b.p. 208° (748 mm.). It freezes at 11°.

This is prepared from o-chlorotoluene by first subjecting it to side-chain chlorination, so as to form o-chlorobenzalchloride, and then hydrolysing the latter compound. The method is described by Erdmann (*Ann.*, 1893, **272**, 151).

The o-chlorotoluene used must be completely dry. 750 gms. of it, to which 23 gms. of phosphorus pentachloride is added, is heated in a flask, with reflux condenser, immersed in an oil-bath at 150° to 180°, preferably in good daylight. A strong stream of *dry* chlorine is passed through in minute bubbles until the increase in weight amounts to about 380 to 400 gms. The product may then be fractionated, the fraction distilling at 226° to 236° being chiefly o-chlorobenzalchloride. This fractionation, however, is unnecessary.

1,100 gms. of the crude chlorobenzalchloride (containing, of course, also chlorobenzylchloride and chlorbenzotrichloride) is added to a mixture of 2,200 gms. of concentrated sulphuric acid and 2,200 gms. of 10 per cent. oleum at ordinary temperature. The chlorobenzalchloride and the trichloride are hydrolysed to aldehyde and carboxylic acid respectively, and these dissolve in the sulphuric acid. The chlorobenzyl chloride and any unchanged chlorotoluene are unaffected and form an oily layer on the surface of the acid. As the hydrochloric acid is evolved, the temperature of the solution falls and after about an hour reaches its minimum, the stream of hydrochloric acid now weakening considerably. After a further hour's stirring, the solution has again reached atmospheric temperature, and at the end of six hours' more stirring the reaction is finished. The mixture is allowed to settle, and the upper oily layer removed. The acid solution is then poured on ice and the oily chlorobenzaldehyde separated. It is washed with dilute sodium carbonate solution, and with water, dried with calcium chloride, and distilled. The yield obtained from 750 gms. of o-chlorotoluene is about 170 gms. of the aldehyde.

(o-Chlorobenzoic acid may be obtained from the dilute acid solution and from the aldehyde wash liquors. It crystallises in large needles, m.p. 140°. 1 part dissolves in 881 parts of water at 0°.)

o-Chlorobenzaldehyde is used in making greenish-blue triphenylmethane dyes by condensation with dialkylanilines or with ethyl-o-toluidine.

2 : 5-**Dichlorobenzaldehyde**—
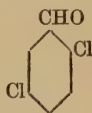
—colourless crystals, m.p. 57° to 58°.

A method of preparing this substance directly from benzaldehyde is described by Gnehm and Bänziger (*Ann.*, 1897, **296**, 62; U.S.P. 315932).

A solution of 10 gms. of iodine in 60 gms. of benzaldehyde is dropped slowly into 540 gms. of antimony pentachloride, stirring the while, the temperature being kept under 60°. When all the benzaldehyde has been added, the mixture is heated at 104° to 105° until no more visible gas is evolved. This takes several hours. The escaping vapours are condensed to recover the iodine. The product is now stirred into 300 gms. of concentrated hydrochloric acid diluted with 600 gms. of water. The oil is separated from antimony chloride solution, and, to remove adhering antimony chloride, is warmed with a very little caustic soda solution and filtered from the precipitated antimony oxide. The alkaline solution is removed, and the oil shaken and heated with 180 gms. of 33 per cent. sodium bisulphite solution diluted with an equal weight of water. The hot solution of bisulphite compound of the aldehyde is separated from undissolved oil, and on cooling sets to a snow-white crystalline mass of the bisulphite compound. This is filtered off and boiled under reflux for some time with 135 gms. of hydrochloric acid. The aldehyde separates as an almost colourless oil, which is removed, dried, and distilled. More of the aldehyde may be obtained by repeated extraction of the residual oil with more bisulphite solution. Distillation of the aldehyde yields a first fraction, up to 231°, containing o- and m-monochloro-benzaldehydes, this being followed by the main quantity at 231° to 238°, consisting of 2 : 5-dichlorobenzaldehyde, and a small third fraction above 238°, containing 3 : 4-dichlorobenzaldehyde.

2 : 5-Dichlorobenzaldehyde may also be prepared from 2 : 5-dichlorotoluene by the method of G.P. 32238 (Badische), which is similar to that by which o-chloro-benzaldehyde is made from o-chlorotoluene.

The 2 : 5-dichlorotoluene required can be obtained by the process described in E.P. 169025 (B.D.C., Green, and Clibbens). 680 gms. of toluene-p-sulphonic acid is neutralised with caustic soda and dissolved in sufficient water to make about 11 litres of solution. Chlorine is passed in until 10 c.c. of the liquid has acquired acidity equivalent to 5·5 c.c. of N/1 alkali. A mixture of the sodium salts of 2 : 5-dichloro- and 2 : 5 : 6-trichlorosulphonic acids is formed, from which, under the conditions stated, nearly all the 2 : 5 : 6-trichlorosulphonate separates in crystalline form. On filtering, and evaporating the filtrate, the 2 : 5-dichlorosulphonate is obtained practically pure. The dichlorosulphonic acid is then hydrolysed in the usual way (p. 127) to obtain 2 : 5-dichlorotoluene.

2 : 5-Dichlorobenzaldehyde is used, like monochlorobenzaldehyde, in making greenish-blue triphenylmethane dyes. These are faster to washing than the corresponding colours from the monochloro compound.

Benzaldehyde-o-sulphonic acid :
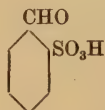
The acid has not been crystallised. The sodium and barium salts crystallise in long prisms.

This substance is most conveniently prepared from o-chlorobenzaldehyde by the action of neutral sodium sulphite, as described in G.P. 88952 (Geigy).

A neutral solution of sodium sulphite is prepared by diluting 50 litres of 40 per cent. bisulphite with 150 litres of water and neutralising with caustic soda, using phenolphthaleïn as indicator. To this is added 20 kg. of o-chlorobenzaldehyde, and the mixture is heated in an autoclave at 170° to 180° for eight hours. The pressure developed is about 8 atmospheres. The solution is now treated with 13 kg. of sulphuric acid and boiled to expel sulphur dioxide and traces of unchanged chlorobenzaldehyde. The sulphonic acid is then isolated either by neutralising with carbonate, evaporating to dryness, and extracting the sodium salt with alcohol, or by forming the barium salt in the ordinary way and evaporating its solution to the crystallising point. The barium salt is rather sparingly soluble.

Benzaldehyde-o-sulphonic acid is used in making a few triphenylmethane dyes by condensation; for example, with benzylethylaniline or with cresotic acid.

The Sulphonation of Toluene.

Toluene is sulphonated at moderate temperatures by concentrated sulphuric acid yielding a mixture of o-, m-, and p-monosulphonic acids in which the p-acid greatly preponderates, while the m-acid is present in very small proportion. The subject has been studied in detail by Hollemann and Caland (*Ber.*, 1911, **44,** 2504). They found that a rise in the temperature of sulphonation favoured the p-acid at the expense of the o-acid, whereas an increased proportion of acid favoured the o-acid at low temperatures. Variation of the concentration of the sulphuric acid from 96 to 100 per cent. had no influence on the proportions of the isomers.

The sulphonation of toluene so as to produce the highest proportion of p-sulphonic acid has been described on p. 127. The p-sulphonic acid can be separated from its isomers by adding to the sulphonation mixture so much water that, on removal of the toluene-p-sulphonic acid, a sulphuric acid of 66 per cent. strength is left, the p-acid being very sparingly soluble in acid of that strength (G.P. 57391), and crystallises out with $1H_2O$. On heating the filtrate to 170° and passing superheated steam at 200°, the remaining o- and m-acids are hydrolysed, and the toluene so formed is recovered. The process is described in greater detail by Inglis (*J. Soc. Chem. Ind.*, 1918, **37,** 288T).

The manufacture of saccharin, for which toluene-o-sulphonic acid is required, led to the development of a procedure by which the maximum proportion of the o-acid could be obtained. It was found that the greatest proportion of o-compound was obtained when toluene was acted on by a large excess of chlorsulphonic acid at low temperatures. A mixture of the sulphonyl chlorides is formed in the proportion of 40 per cent. of the o- to 60 per cent. of the p-compound. Excess of chlorsulphonic acid (about 4 molecules to 1 molecule of toluene) is required in order to avoid formation of toluenesulphonic **acid** by a secondary reaction, thus :

$$(a)\ \ C_7H_8\ +\ Cl.SO_3H\ \longrightarrow\ C_7H_7.SO_2Cl\ +\ H_2O$$

$$(b)\ \ C_7H_7.SO_2Cl\ +\ H_2O\ \longrightarrow\ C_7H_7.SO_3H\ +\ HCl$$
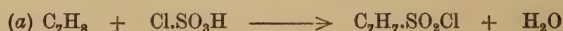
The procedure, as described by Gilliard, Monnet, and Cartier (G.P. 98030), is as follows : Into 400 kg. of chlorsulphonic acid, stirring at 0°, is run slowly 100 kg. of

toluene, the temperature being kept under 5°. The mixture is stirred for twelve hours more, keeping within the same temperature limits of 0° to 5°. It is then poured on ice, when the mixture of sulphonyl chlorides separates in liquid condition. The acid layer is removed by decantation, and the chlorides washed with water. The mixture is then cooled to − 20°, and after twelve hours at this temperature most of the p-sulphonyl chloride has crystallised out, and this is separated by filtration or by centrifuging. The remaining liquid, amounting to about 60 per cent. of the original total, is composed of 70 per cent. o-compound, and 30 per cent. p-compound. A further separation is described in G.P. 95338 (Majert and Ebers). The liquid is distilled under reduced pressure until about 30 to 40 per cent. has passed over. This fraction is almost pure o-sulphonyl chloride. The residue is then frozen again at − 20°, when more of the p-sulphonyl chloride crystallises out and is filtered off. The treatment is repeated with the mother liquor.

The **toluene-p-sulphonyl chloride** thus obtained as a by-product of saccharine manufacture has become a useful reagent in several ways in the preparation of dyestuff intermediates. By acting on it with methyl and ethyl alcohols, **toluene-p-sulphonic methyl** and **ethyl esters** are obtained, which are used as alkylating agents. Again, by stirring the sulphonyl chloride with concentrated aqueous ammonia, **toluene-p-sulphonamide** is formed, which Ullmann has shown can be used effectively in converting chloroanthraquinones into the corresponding aminoanthraquinones (p. 222).

XYLENE DERIVATIVES

THE xylene derivatives are obtained from commercial "pure xylene," a mixture of the three xylenes which boils between 138° and 142°. It contains usually about 60 per cent. of *m*-xylene, and quantities of *o*- and *p*-xylenes, each varying between 10 and 25 per cent. A little ethylbenzene is also present.

Nitroxylenes.—The xylenes are not usually separated. The mixture is nitrated by the same process as that used for nitrobenzene (p. 16), though the temperature should be kept lower (about 20°) during nitration in order to avoid oxidation of the methyl groups. A mixture of five mononitroxylenes is thus obtained, whose properties are given in the following table :

	Constitution.			*Melting-Point.*	*Boiling-Point.*	*Specific Gravity.*
	CH_3	CH_3	NO_2			
3-Nitro-*o*-xylene ..	1	2	3	7° to 9°	245° to 246° (760 mm.)	1·147 at 15°
4-Nitro-*o*-xylene ..	1	2	4	30°	258° (748 mm.)	1·139 ,, 30°
2-Nitro-*m*-xylene ..	1	3	2	Liquid	225° (744 mm.)	1 112 ,, 15°
4-Nitro-*m*-xylene ..	1	3	4	20°	244° (760 mm.)	1·135 ,, 15°
2-Nitro-*p*-xylene ..	1	4	2	Liquid	239° (739 mm.)	1·132 ,, 15°

The sixth possible nitroxylene, 5-nitro-*m*-xylene, is not formed in this way.

Xylidines.—The nitroxylenes are not separated, but are reduced directly to the xylidines by iron and hydrochloric acid, as in the preparation of aniline from nitrobenzene (p. 26). The five xylidines so formed have the following properties :

	Melting-Point.	*Boiling-Point.*	*Specific Gravity at 15°.*	*Melting-Point of HCl Salt.*	*Melting-Point of Acetyl Derivative.*
o-3-Xylidine.. ..	Liquid	223°	0·991	254°	134°
o-4-Xylidine.. ..	49°	226°	1·0755	256°	99°
m-2-Xylidine ..	Liquid	216°	0·980	—	176·5°
m-4-Xylidine ..	Liquid	212°	0·9184	235°	129°
p-Xylidine	15·5°	215°	0·980	228°	139·5°

The mixed xylidines are used to some extent for monoazo dyes, in which the diazo compounds are coupled with β-naphthol and its sulphonic acids as second components.

Separation of the Xylidines.

The chief constituents of the xylidine mixture are *m*-4-xylidine (usually referred to simply as *m*-xylidine), which forms about half of the mixture, and *p*-xylidine, which is present to the extent of 10 to 20 per cent. These two xylidines are separated from the mixture by one of the following methods.

m-**Xylidine :**

CH_3

CH_3

NH_2
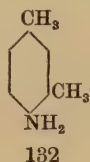
This is best separated by the method described in G.P. 39947 (Limpach). 121 parts of the xylidine mixture and 30 parts of glacial acetic acid are mixed and allowed to stand for a day or two. *m*-Xylidine acetate alone crystallises out. The crystals are separated by centrifuging.

p-**Xylidine** :

CH₃
NH₂
CH₃
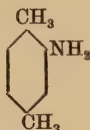
A crude *p*-xylidine is obtained from the mother liquor remaining after the separation of *m*-xylidine acetate, by adding to it 1 molecular proportion of hydrochloric acid. *p*-Xylidine hydrochloride crystallises out, and after a few days is separated by centrifuging. The crude base is recovered from its salt in the usual way.

From this crude base pure *p*-xylidine can be obtained by the method of G.P. 71969 (Bayer). 121 parts of the crude base are mixed with 106 parts of benzaldehyde. The mixture heats up to about 60° and water separates, owing to the formation of the benzylidene derivatives of the bases :

$$C_6H_3(CH_3)_2NH_2 \ + \ C_6H_5.CHO \ \longrightarrow \ C_6H_3(CH_3)_2N:CH.C_6H_5 \ + \ H_2O$$

To some extent, however, the reaction takes another course, *pp′*-diaminodi-*p*-xylyl-phenylmethane being formed :

CH₃   CH₃
H₂N   NH₂
CH₃ CH CH₃
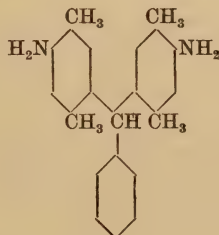
The water is separated either by long standing of the mixture in tall narrow vessels or by slow evaporation. The oil sets to a crystalline mass on cooling, the crystallisation being complete in twenty-four hours. The crystals are separated by centrifuging and pressing from the residual oil, and are washed with alcohol. The pure benzylidene compound of *p*-xylidine is thus obtained as pale yellow crystals, m.p. 102° to 103°. It is decomposed by heating with dilute mineral acid, and the liberated benzaldehyde is distilled off with steam. The remaining solution is then made alkaline with caustic soda or milk of lime, and the *p*-xylidine distilled in steam.

The diaminodixylylphenylmethane remains in the alkaline liquid, as it is not volatile in steam.

Applications of the Xylidines.

m-Xylidine is used as a first component in azo dyes, in which its diazo compound is coupled with β-naphthol or the naphtholsulphonic acids.

p-Xylidine, on the other hand, is chiefly used as a middle component in dis- and

trisazo dyes. It couples readily with diazo compounds, and the free amino group in the resulting aminoazo compound can then be diazotised and coupled with a third component.

m-**Xylidine**-*o*-**sulphonic acid** :
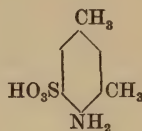
This acid may be prepared by the procedure described in E.P. 175019 (B.D.C., Baddiley, Payman, and Wignall). Sulphonation with chlorsulphonic acid in an organic solvent is found to introduce a sulphonic acid group in the *o*-position to the amino group.

121 gms. of *m*-xylidine is dissolved in 500 gms. of tetrachlorethane, and to the stirred solution 122 gms. of chlorsulphonic acid is slowly added, the temperature being allowed to rise to 80°. The solution is then gradually heated to the boiling-point, and is boiled under reflux until the evolution of hydrochloric acid ceases. After cooling, the *m*-xylidinesulphonic acid is extracted with aqueous alkali, and the free acid precipitated by acidifying with hydrochloric acid.

m-Xylidine-*o*-sulphonic acid is used as first component in an azo dye, Normal Yellow 3GL, of which a pyrazolone derivative is second component.

Dehydrothio-*m*-**xylidine**—
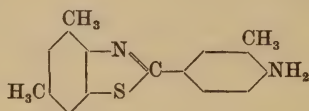
—crystallises from alcohol in prisms, m.p. 107°, b.p. 282° to 284° (13 to 14 mm.). It is insoluble in water, very soluble in hot alcohol, and sparingly soluble in cold alcohol. The acetyl derivative melts at 227°.

This is prepared, like dehydrothiotoluidine, by heating *m*-xylidine (6 parts) with sulphur (1 part) at 180° to 200° until evolution of hydrogen sulphide ceases. The excess of xylidine is distilled off. The residue contains, besides dehydrothio-*m*-xylidine, an isomeric body named *iso*dehydrothio-*m*-xylidine :
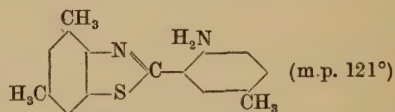
The two are separated by extracting the mixture with 30 per cent. hydrochloric acid, in which the *iso*base is insoluble.

Dehydrothio-*m*-xylidine is used, like dehydrothiotoluidine, as first component in several monoazo dyes, the second components being α- and β-naphtholsulphonic acids.

NAPHTHALENE DERIVATIVES: A PRELIMINARY SURVEY

In the preparation of dyestuff intermediates from naphthalene, the general aim, as with intermediates from other sources, is to introduce the auxochrome groups, amino and hydroxyl, accompanied by sulphonic acid groups to confer solubility on the products or to occupy certain positions in the molecule in order to exclude the formation of undesired isomers during the preparation of dyestuffs from the intermediates. Up to the present, therefore, the naphthalene derivatives which have been made have been of the nature of naphthylamines, naphthols, aminonaphthols, and their sulphonic acids, with the addition of a few naphtholcarboxylic acids. These substances have been used almost exclusively as intermediates for azo dyes, for which they are peculiarly suited, and on their usefulness for this purpose depends the great preponderance of azo dyes as compared with other classes. About 600 of the 1,200 dyestuffs mentioned in the Colour Index belong to the azo class.

The methods used for the preparation of these intermediates involve the operations of (1) sulphonation, (2) nitration, (3) hydrolysis with alkalies, and (4) replacement of the amino group by hydroxyl, or of hydroxyl by amino, by the aid of sulphites, this last being known as the Bucherer reaction. It is somewhat remarkable that, up to the present, chlorination has played no part in the preparation of these compounds, although a number of chloro derivatives have been made, and it is known that the chlorine atom in such compounds can be replaced by hydroxyl under the action of alkalies.

I. Sulphonation of Naphthalene.

The fundamental work on the sulphonation of naphthalene was carried out by Armstrong and Wynne (whose results are mentioned, with little detail, in the Proceedings of the Chemical Society, 1885 to 1895), and by Merz, Ebert, and collaborators. Valuable additions to our knowledge in this field have also been made later by Euwes (1909), Witt (1915), and recently by Fierz-David in a number of papers in *Helvetica Chimica Acta* (1920 to 1923).

Considering the number of isomers theoretically possible in the case of the polysulphonic acids, it is fortunate that actually the number of isomers formed is much limited according to the rule, established by Armstrong and Wynne, that a second sulpho group never enters the ortho, para, or peri position to the first. It has also been established that when two sulpho groups are introduced, they enter different nuclei in the naphthalene molecule.

(*a*) **Monosulphonic Acids.**—Naphthalene is sulphonated rather easily by concentrated sulphuric acid to a mixture of the α- and β-sulphonic acids. The proportion of each isomer formed depends on the temperature of sulphonation, but under no conditions is either isomer obtained as the sole product. The addition of mercury salts to the reaction mixture has no appreciable influence on the proportions of the isomers. Low temperatures favour the formation of the α-acid, while high tempera-

tures favour the β-acid. At temperatures under 40°, the sulphonation product contains about 96 per cent. of the α-acid and 4 per cent. of the β-acid. At 160° to 165°, the proportions are 85 per cent. of the β-acid and 15 per cent. of the α-acid. This is the highest porportion of the β-acid so far obtainable.

(*b*) **Disulphonic Acids.**—In conformity with the rules given above, only four disulphonic acids are formed by the direct sulphonation of naphthalene or naphthalene-monosulphonic acids. These are the 1 : 5-, 1 : 6-, 2 : 7-, and 2 : 6-disulphonic acids :*

1 : 5-acid.　　　　1 : 6-acid.　　　　2 : 7-acid.　　　　2 : 6-acid.
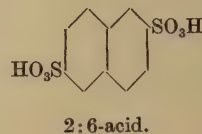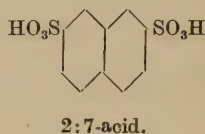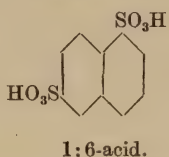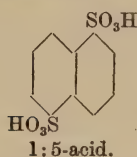
An elaborate investigation of the disulphonation of naphthalene made by Fierz-David and Hasler (*Helv. Chim. Acta*, 1923, **6**, 1133) has led to the following conclusions : Under 40°, almost constant proportions of the 1 : 5- and 1 : 6-acids, about 70 per cent. of the 1 : 5- and 25 per cent. of the 1 : 6-, are formed, together with traces of the 2 : 7-acid. As the temperature of sulphonation is raised, the proportion of 1 : 5-acid diminishes, owing to replacement by 1 : 6- and 2 : 7-acids, and at 130° to 135° the 1 : 5-acid is not present in the mixture. At 140°, the 2 : 6-acid begins to appear, and increases in proportion as the temperature rises, until at 180° a maximum proportion of about 30 per cent. is reached, the other components being the 1 : 6- and 2 : 7-acids. At 165°, the mixture contains about 25 per cent. of the 2 : 6-acid, 65 per cent. of the 2 : 7-acid, and 10 per cent. of the 1 : 6-acid.

(*c*) **Trisulphonic Acids.**—Only three trisulphonic acids are possible by the Armstrong-Wynne rule—namely, the 1 : 3 : 5-, 1 : 3 : 6- and 1 : 3 : 7-acids :

1 : 3 : 5-acid.　　　　1 : 3 : 6-acid.　　　　1 : 3 : 7-acid.
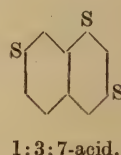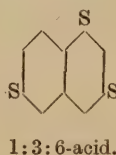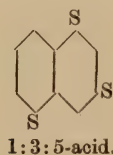
Of these, the 1 : 3 : 5- and 1 : 3 : 6-acids only are of importance for the preparation of dyestuff intermediates, the 1 : 3 : 6-acid being by far the more important as intermediate for H-acid. The 1 : 3 : 5-acid can obviously only be formed from the 1 : 5-disulphonic acid. The 1 : 3 : 6-acid is formed both from the 1 : 6- and from the 2 : 7-disulphonic acid, and is the only possible trisulphonic acid from either :
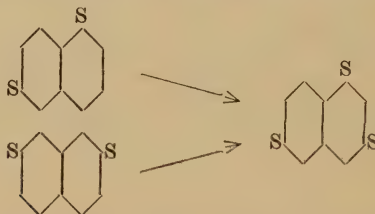
* The 1 : 7-acid is also possible under the rule, but apparently is not formed.

It is of interest also that the 1 : 3 : 6-acid cannot be sulphonated further. Only one tetrasulphonic acid, the 1 : 3 : 5 : 7-acid, has been definitely proved to be formed, and this is formed from either the 1 : 3 : 5- or the 1 : 3 : 7-trisulphonic acid.

The following scheme, given by Fierz-David (*J. Soc. Chem. Ind.*, 1923, **42**, 421T), shows in graphic form the relations between the various sulphonic acids :

40°C. 160°C.

96% + 4% 15% + 85%

40°C. 160%C.

65–70% 30–35% 75–80% 20–25%

100% 95% 100%

100%
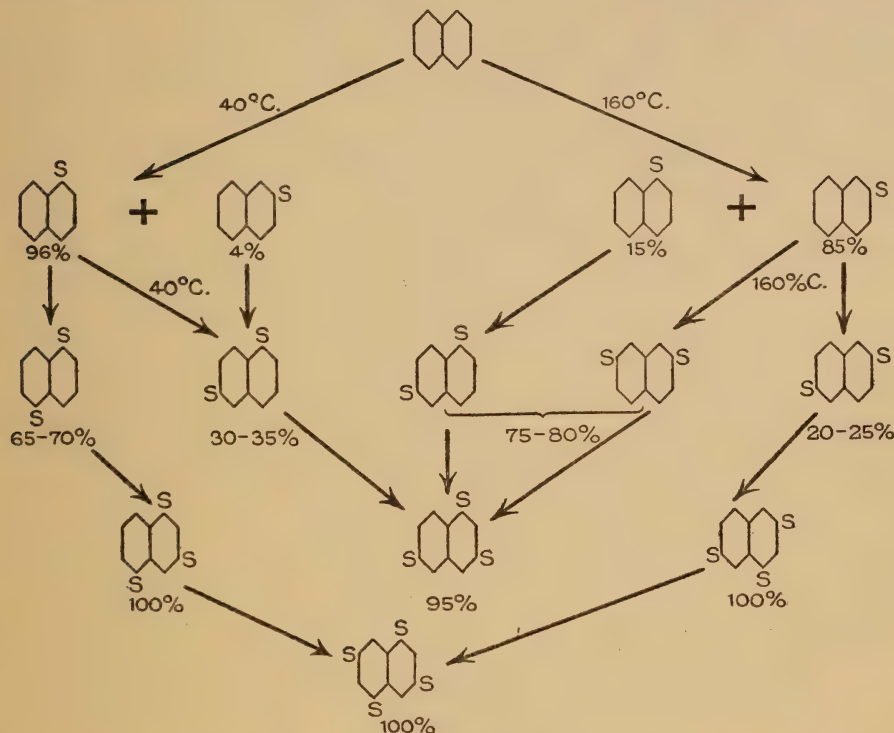
II. Nitration of Naphthalene and Its Sulphonic Acids.

Naphthalene, when nitrated, gives almost exclusively the α-nitro derivative, only traces of the β-nitro derivative being formed. On further nitration, the 1 : 5- and 1 : 8-dinitro derivatives are obtained in the proportion of 1 to 2. The tri- and tetranitro derivatives have not been used for dyestuff intermediates. On reduction, the nitro compounds yield the amines, but only α-naphthylamine is of importance as a dyestuff intermediate, the 1 : 5- and 1 : 8-diamines not being used. As β-nitro-naphthalene is not formed by direct nitration of naphthalene, β-naphthylamine is prepared by another method.

When the naphthalenesulphonic acids are nitrated, the nitro group again enters an α-position, but not quite so exclusively as in the case of naphthalene itself. Small proportions of β-nitro derivatives are formed, the more the higher the temperature of nitration. Fierz-David has found that, using the calculated quantity of nitric acid for mononitration, an appreciable proportion of sulphonic acid, 4 to 14 per cent., always escapes nitration, and if excess of nitric acid is used, dinitro compounds are

formed. This is one of the main causes of the comparatively low yields obtained of the ultimate naphthylaminesulphonic acids prepared in this way.

Naphthalene-α-sulphonic acid, on nitration, yields 60 to 70 per cent. of the 1 : 8- and 30 to 40 per cent. of the 1 : 5-nitrosulphonic acids. If, on the contrary, α-nitronaphthalene is sulphonated, an 80 per cent. yield of the 1 : 5-nitrosulphonic acid may be obtained, along with some 1 : 6- and 1 : 7-nitrosulphonic acids.

Nitration of naphthalene-β-sulphonic acid gives 40 to 50 per cent. of the 1 : 6-, and about 40 per cent. of the 1 : 7-nitrosulphonic acids, along with a little of the 1 : 3-acid.

The products of nitration of the di- and trisulphonic acids are as follows :

60 to 70 per cent.   About 30 per cent.

43 per cent.   15 per cent.   + Unknown products

+ a little O₂N ... S (?)
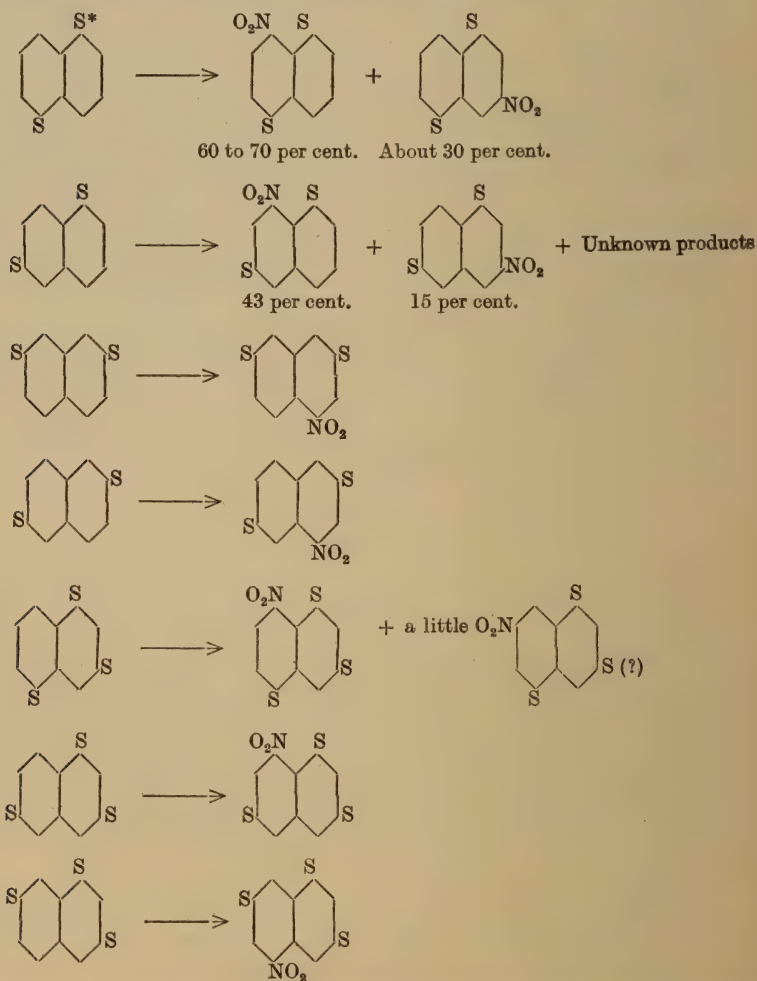
In ordinary practice the nitronaphthalenesulphonic acids are not isolated, but are reduced directly to the desired naphthylaminesulphonic acids.

* SO₃H is here abbreviated to S for convenience.

III. Hydrolysis of Naphthalene Derivatives.

Alkali fusion of the naphthalenesulphonic acids takes the normal course, and α- and β-naphthols are prepared in this way from the monosulphonic acids. In the case of α-naphthol, however, another method is available for its preparation, since α-naphthyl-aminesulphate is hydrolysed by water at 200° to α-naphthol, and a pure product free from β-naphthol is obtained by this method. The disulphonic acids yield the dihydroxynaphthalenes by alkali fusion, but of these only the 1 : 5-compound is of importance. By heating the di- and trisulphonic acids with concentrated solutions of alkali at temperatures of 200° and over in autoclaves, one sulpho group may be replaced, yielding naphtholsulphonic acids. In this way 2-naphthol-7-sulphonic acid (F-acid) is prepared from the 2 : 7-disulphonic acid. But all the other β-naphthol-sulphonic acids are prepared by the sulphonation of β-naphthol, and most of the α-naphtholsulphonic acids are prepared from the corresponding naphthylamine-sulphonic acids by heating their diazonium sulphates or otherwise.

Heating with concentrated aqueous alkali in autoclaves is used in the case of naphthylaminesulphonic acids to replace one sulpho group by hydroxyl, thus yielding aminonaphtholsulphonic acids. In this way 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) is prepared from 1-naphthylamine-3 : 6 : 8-trisulphonic acid, as are also 1 : 8-aminonaphthol-4 : 6-disulphonic acid (K-acid), 1 : 8-aminonaphthol-4-sulphonic acid (S-acid), 1 : 8-aminonaphthol-2 : 4-disulphonic acid (2S-acid), 2-amino-5-naphthol-7-sulphonic acid (J-acid), 2-amino-8-naphthol-6-sulphonic acid (Gamma acid), and a few others, from the corresponding naphthylaminesulphonic acids.

In such cases, however, the reaction can proceed further to replace the amino group also by hydroxyl. Thus H-acid and S-acid may be further hydrolysed to 1 : 8-dihydroxy-3 : 6-disulphonic acid (Chromotrope Acid) and 1 : 8-dihydroxynaphthalene-4-sulphonic acid (Dioxy-S-acid) respectively.

IV. The Bucherer Reaction.

It has been mentioned that the amino group in naphthylamine derivatives can often be replaced by hydroxyl through the action of water or alkalies at high tempera-tures. H. T. Bucherer (*J. pr. Chem.*, 1904, [2], **69,** 88) discovered that this replacement was much facilitated by the use of sulphites, and that, in addition, the reverse replacement of hydroxyl by the amino group, which can be accomplished sometimes by heating at high temperatures with ammonia, can be carried out more easily in presence of sulphite. The action of the sulphite is not catalytic in the ordinary sense. It must be used in molecular quantities, sometimes in large excess, and intermediate compounds are formed (these have been isolated in many cases), which Bucherer regards as the sulphurous esters of the **naphthols,** whether the starting material is a naphthol or a naphthylamine derivative :

$$R.OH \qquad\qquad R.NH_2$$
$$+ NaHSO_3$$
$$R.O.SO_2Na$$
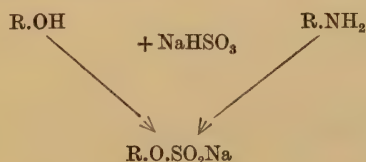
This view of their constitution has been controverted by Voroschćov (*J.C.S. Abstr.*, 1916, i., 293), and Friedländer (*Ber.*, 1921, **54**, 620-624), who regard them as bisulphite compounds of the ketonic forms of the naphthols :
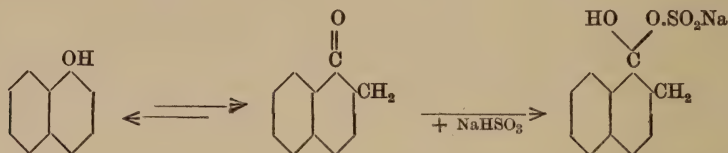
The former obtains support for his view from the analysis of the isolated intermediates in some cases.

The important consideration, however, in connection with the naphthalene derivatives in question, is the properties of these intermediates. They are fairly stable in neutral or acid solution, though some are partially hydrolysed to naphthol and bisulphite, but they are very sensitive to caustic alkalies and even to carbonates, being quickly and completely hydrolysed to naphthol and sulphite, even at comparatively low temperatures. By ammonia, on the other hand, they are easily converted into naphthylamine. On Bucherer's view, therefore, the reactions may be summarised as follows :

$$R.OH \underset{+ \text{ alkali}}{\overset{+ \text{ bisulphite}}{\rightleftarrows}} R.O.SO_2Na \underset{+ \text{ bisulphite}}{\overset{+ \text{ NH}_3}{\rightleftarrows}} R.NH_2$$
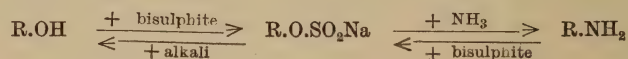
The method has proved exceedingly useful and economical. β-Naphthylamine, for example, which had previously been made by heating β-naphthol with ammonia solution at 200° for a day, under very high pressure, could now, by Bucherer's method, using ammonium sulphite and ammonia, be formed by heating at 150° for eight hours at 6 atmospheres pressure, and obtained in better yield and purer condition. An example of the reverse change is the preparation of 1-naphthol-4-sulphonic acid from 1-naphthylamine-4-sulphonic acid (naphthionic acid) by heating with sodium bisulphite followed by hydrolysis with alkali.

The reaction is not quite generally applicable. Sulphonic acids of α-naphthol containing sulpho groups in the ortho or meta position to the hydroxyl, and β-naphtholsulphonic acids in which there is a sulpho group in the 4- or meta position, do not give the reaction. They do not even form the intermediate sulphurous esters.

NITRONAPHTHALENES AND THEIR DERIVATIVES

Naphthalene—

—a white crystalline solid, m.p. 80·1°, b.p. 218°. The specific gravity compared with water at 0° is as follows : 1·1517 at 15°, 1·1508 at 18°, 0·9778 at 79·2°, 0·9628 at 100°.

It sublimes readily, and is volatile in steam and in alcohol vapour. It is insoluble in cold water, but hot water dissolves traces of it. It is soluble in alcohol, ether, acetic acid, benzene and its homologues, and very soluble in phenols. At 15°, 100 parts of alcohol dissolve 5·29 parts of naphthalene, but at the boiling-point of alcohol the two are miscible in all proportions. At 15·5, 100 parts of benzene, toluene, or xylene dissolve 45·8, 32·0, and 31·5 parts respectively of naphthalene. Molten naphthalene dissolves sulphur, metallic sulphides, and Indigo.

The commercial naphthalene used for the manufacture of dyestuff intermediates is required to reach a high standard of purity. It should be white, and should leave no residue on volatilisation. The setting-point (this is determined in preference to the melting-point) should be 79·6° to 79·8°. Heated with concentrated sulphuric acid it should dissolve to a clear solution, almost colourless, at the most slightly pink at water-bath temperature, or light brown at 180°. The solution on dilution and making alkaline with caustic soda should give no smell of pyridine bases, and on addition of bromine water and hydrochloric acid to the filtered alkaline extract should give no clouding due to bromophenols.

α-Nitronaphthalene—
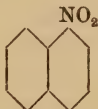
—crystallises in yellow needles, m.p. 61°, b.p. 304°, D^4 1·331. 100 parts of alcohol (87·5 per cent.) at 15° dissolve 2·8 parts. It dissolves to a blood-red solution in sulphuric acid.

The nitration of naphthalene may be carried out at moderate temperatures with fairly dilute mixed acid. In fact, in the preparation of the mononitro compound, the maximum dilution is used in order to avoid formation of dinitro derivatives. The manufacture of α-nitronaphthalene, as described by Witt (*Chem. Ind.*, 1887, **10,** 216), gives a product of satisfactory purity in almost quantitative yield.

1,000 parts of mixed acid of the approximate composition—

HNO_3	..	..	..	..	..	..	12·5 per cent.
H_2SO_4	..	..	..	..	..	..	58·0 ,,
H_2O ..	..	..	..	..	..	..	29·5 ,,

—is stirred and heated to 45°. 250 parts of very finely powdered naphthalene is added gradually through a sieve in order to avoid formation of clumps. The tem-

perature is then maintained at 45° to 50° until the nitration is finished, which takes about a day. The nitro compound separates, as semisolid clumps on the surface of the acid. The spent acid is run off, and the nitro compound well washed with boiling water to remove acid. It is finally granulated by running the molten substance into vigorously stirred cold water. The product so obtained contains about 95 per cent. of α-nitronaphthalene, together with a little dinitro compound, unchanged naphthalene and traces of the β-nitro compound. It is pure enough for its sole usual application—namely, reduction to α-naphthylamine. But it may be purified by melting it up with about a tenth of its weight of cumene or solvent naphtha and allowing to crystallise.

The spent acid has the composition : 1 per cent. HNO_3, 65 per cent. H_2SO_4, 34 per cent. H_2O, and, of course, can be used for a fresh charge by making up to the required strength with 60 per cent. nitric acid and ordinary concentrated sulphuric acid.

α-**Naphthylamine**—

—crystallises in colourless scales or flat needles, m.p. 50°, b.p. 300·8°, D_{20}^{20} 1·171. It is almost insoluble in water, 100 c.c. of water at ordinary temperature dissolving 0·167 gm. It is easily soluble in alcohol and ether.

Its salts are rather sparingly soluble in water, especially the **sulphate,** $(C_{10}H_7NH_2)_2.H_2SO_4+2H_2O$, which crystallises in white scales, sparingly soluble in cold water and alcohol, but easily in hot water. The **hydrochloride,** $C_{10}H_7NH_2.HCl$, forms long needles, soluble in alcohol, but 100 parts of water at 20° dissolve 3·77 parts.

Its **acetyl** derivative, $C_{10}H_7.NH.CO.CH_3$, forms needles, m.p. 159°.

The usual method of preparation is by reduction of the nitro compound with iron borings and a little hydrochloric acid, as in the preparation of aniline. In this case, however, the reduction mixture is not boiled. The reaction is so vigorous, and the tendency towards elimination of the amino group during reduction is so great, that the reduction is usually carried out at about 50°. Even then, there is always some naphthalene formed.

Continuing the description of the process given by Witt (see under α-Nitronaphthalene), 800 parts of iron borings, 40 parts of concentrated hydrochloric acid, and 400 parts of water are stirred in an iron vessel (no reflux) and heated to 50°. 600 parts of the air-dried crude nitronaphthalene are added gradually, the temperature being maintained about 50°. A fairly vigorous reaction occurs. About six or eight hours are required to complete the reduction. A sample should be almost entirely soluble in dilute hydrochloric acid. The mixture is now made alkaline with milk of lime made from 50 parts of lime, or with soda. The separation of the α-naphthylamine from the sludge of iron oxide, iron, etc., in an economical manner, has always been a difficult problem to which no absolutely satisfactory solution seems to have been found. Distillation of the base in superheated steam is apparently the best method, but the high temperature required causes further side reactions, particularly reduction
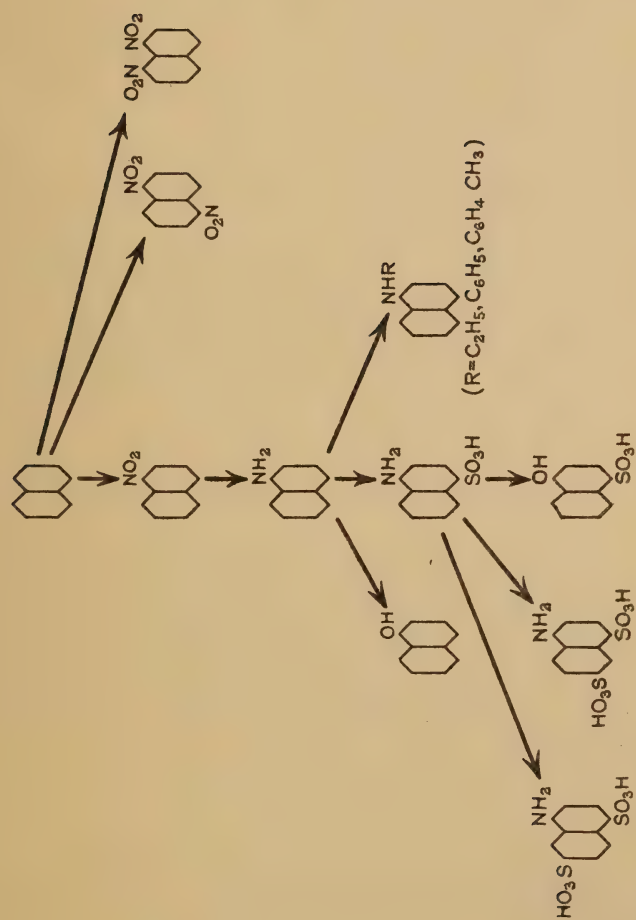
CHART VII.—NITRONAPHTHALENES AND THEIR DERIVATIVES.

to naphthalene. The contents of the reduction vessel having been transferred to a suitable still and heated to about 200°, superheated steam at 250° is passed through, the mixture being stirred continuously. Each part of steam carries over $\frac{1}{2}$ to 1 part of naphthylamine. Some iron powder and oxide is also carried over, and the product collects as a black oil or solid. (The residue in the still contains pyrophoric iron.) This is separated from the water and distilled in a vacuum, when the base is obtained as a water-white oil, which crystallises on cooling. The yield of α-naphthylamine is about 110 parts, or an overall yield of about 77 per cent. on the naphthalene used. The chief source of loss is the steam distillation. The commercial product always contains a little naphthalene, as shown by the fact that a small proportion of it is insoluble in dilute hydrochloric acid. The naphthalene present can be estimated by distilling the acid solution with steam and extracting the aqueous distillate with ether. The base itself is estimated by titration with nitrite, checked by coupling the diazo compound with Schäffer salt.

α-Naphthylamine is used as a first component in a number of important monoazo dyes. It can also serve as a middle component, since it couples readily, in the *p*-position to the amino group, with diazo compounds, and the resulting aminoazo dyes can be diazotised and coupled with a third component. Dyes of very deep blue or black shades are produced in this way, as for instance the Coomassie Navy Blues and Victoria Black.

A few basic dyes of the azine and oxazine series are made from α-naphthylamine by condensing it with *p*-nitrosoalkylanilines or with nitroso derivatives of the dialkyl-*m*-aminophenols.

Secondary Bases from α-Naphthylamine.

These are made partly for use as end components in azo dyes, but more especially for the preparation of naphthalene analogues of the triphenylmethane colours. Like the alkylanilines, they condense with Michler's ketone or hydrol in the *para* position to the amino group, yielding blue basic dyes, such as Victoria Blues B and R.

Ethyl-α-naphthylamine—

—a colourless oil which quickly turns blue in air. B.p. $_{776}$ 325° to 330°, b.p. $_{26}$ 191°.

This substance is made by ethylating α-naphthylamine with ethyl alcohol and hydrochloric acid, as in the preparation of ethylaniline (p. 46), or with ethyl chloride.

Phenyl-α-naphthylamine—
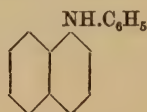
—crystallises in prisms, m.p. 62°, b.p. $_{258}$ 325°, b.p. $_{15}$ 226°. It is soluble in alcohol, ether, and benzene, the solutions showing blue fluorescence. It is a comparatively weak base, and is insoluble in dilute acids.

For its preparation, α-naphthylamine and aniline are heated together, and Knoevenagel's method of accelerating the reaction with iodine (*J. pr. Chem.* [2], **89**, 20) gives the best results. The method is described in G.P. 241853 (Knoll and Co.). Equimolecular quantities of α-naphthylamine and aniline are heated with about 1 per cent. of iodine (calculated on the aniline) for six hours at 230°, and then for two hours at 250°. The product is washed with dilute hydrochloric acid, then with water, dried and distilled in a vacuum. The yield is given as 85 per cent.

p-**Tolyl-α-naphthylamine**—
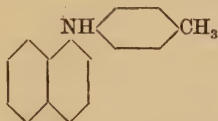
—crystallises in prisms, m.p. 78°, b.p.$_{15}$ 236°. It is soluble in ether and alcohol, and is best crystallised from alcohol. The solutions show blue fluorescence.

It is prepared, by a method similar to that used for phenyl-α-naphthylamine, by heating α-naphthylamine with *p*-toluidine and iodine. A somewhat higher temperature, 260° to 270°, is used and the condensation is not quite so complete, the yield obtained being about 70 per cent.

α-**Naphthol**—

—crystallises in lustrous needles, m.p. 94°, b.p. 278° to 280°, D^4 1·224. It is only slightly soluble in water, but dissolves in alcohol, ether, and benzene, and also in solutions of caustic alkalies. It is volatile in steam.

α-Naphthol is prepared by hydrolysis of salts of α-naphthylamine at high temperatures, as described in G.P. 74879 (Meister Lucius and Brüning). The sulphate is usually employed:

$$(C_{10}H_7.NH_2)_2H_2SO_4 \;+\; 2H_2O \;\longrightarrow\; 2C_{10}H_7.OH \;+\; (NH_4)_2SO_4$$

Fierz-David ("Farbenchemie," 1920, p. 127) gives the process in detail. 143 gms. of α-naphthylamine is melted in 1 litre of hot water in a lead-lined or enamelled autoclave provided with a stirrer. 110 gms. of concentrated sulphuric acid is added in a thin stream, with stirring. The mixture is then heated at 200° for eight hours, the pressure developed being 14 atmospheres. After cooling, the naphthol is separated from the aqueous solution of ammonium sulphate, and purified by melting up with a little water. After solidifying again, it is separated from the water and dried. A very pure product is obtained, the yield being 94 to 95 per cent.

α-Naphthol may also be prepared, and more cheaply, from naphthalene-α-sulphonic acid (p. 152), but the product obtained in this way always contains β-naphthol, and if a pure α-naphthol is required the above process is preferable.

A nitro dye, Martius Yellow, is made by nitrating α-naphthol. Again, by sulphonating α-naphthol to its 2 : 4 : 7-trisulphonic acid and nitrating this, which

10

displaces the sulpho groups in the 2- and 4-positions by nitro groups, Naphthol Yellow S is obtained.

α-Naphthol is also used as second component in a number of monoazo dyes.

It condenses with *p*-nitrosodimethylaniline to form an indophenol, a rather unstable vat dye similar to Indigo in shade.

Naphthionic acid :
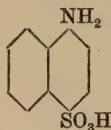
The acid crystallises in small lustrous needles with $\frac{1}{2}H_2O$, and is very sparingly soluble in water. It dissolves in 3,225 parts of water at 20°, and in 438·5 parts at 100°.

The sodium salt crystallises in large prisms with $4H_2O$, and is readily soluble in water, as are also the calcium and barium salts. The solutions, when dilute, show blue fluorescence.

The acid is hydrolysed by steam at 180° to α-naphthylamine.

While naphthionic acid may be prepared by sulphonating α-naphthylamine in the usual way by heating it with three times its weight of 94 per cent. sulphuric acid at 130°, the ordinary method is to bake α-naphthylamine sulphate at 170° to 180°. The remarks made with regard to this process in connection with sulphanilic acid apply in this case also. That is, the proportion of sulphuric acid used should be exactly that required to form the sulphate, and iron salts should be excluded. The best results seem to be obtained by the process described by Schultz ("Chemie des Steinkohlenteers," third edition, p. 202).

50 kg. of α-naphthylamine is melted and at 60° 36·5 kg. of 94 per cent. sulphuric acid stirred in. The mass becomes pasty. It is slowly heated, with continuous stirring, to 170° to 180°, when it becomes fluid and homogeneous. It is now vigorously stirred and $2\frac{1}{2}$ kg. of powdered crystalline oxalic acid added, the effect of which is to " blow up " the mass and make it porous. It is spread evenly on lead plates and heated in an oven (preferably a vacuum oven) at 170° to 180°, with careful temperature regulation, for eight hours. The product contains, besides naphthionic acid, about 3 to 7 per cent. of α-naphthylamine-5-sulphonic acid (Laurent's acid), and usually also some α-naphthylamine. It is powdered, boiled up with water, and neutralised with milk of lime. The mixture is filtered hot, the residue being well washed out with boiling water, and the naphthionic acid is precipitated from the filtrate by addition of hydrochloric acid. It is filtered off, washed with cold water, and dried. The yield of crude acid is 64 kg. or about 80 per cent.

It is purified by dissolving in the minimum quantity of hot water and soda, extracting any α-naphthylamine present with solvent naphtha, and allowing the sodium naphthionate to crystallise out. The more soluble sodium salt of Laurent's acid remains in solution.

Naphthionic acid is used as an intermediate for azo dyes. It may function both as a first component and as an end component. In the former case, coupled with the

naphthols and their sulphonic acids, it yields the Fast Reds, a series of monoazo dyes for wool characterised by good fastness to light.   In the latter case, it is coupled with diazotised diamines of the benzidine type to produce the Congo Reds and Benzopurpurins, direct cotton colours of bright shades, but very sensitive to acids.

α-**Naphthol**-4-**sulphonic acid** (NW-acid):

$$\text{OH} \\ \text{SO}_3\text{H}$$
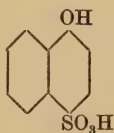
The acid crystallises in transparent plates, soluble in water.   With ferric chloride its solution gives a blue colouration, changing to red on warming.   The sodium salt is also soluble in water, but can be salted out from concentrated solutions.   It is soluble in 90 per cent. alcohol.   The other salts are easily soluble in water.

This acid was originally obtained from naphthionic acid by Neville and Winther (*J.C.S.*, 1880, **37,** 632).   The naphthionic acid is first diazotised, and the sparingly soluble diazo compound as a thin paste with water is run into a boiling 4 per cent. solution of sulphuric acid :

$$\begin{array}{ccccc} \text{NH}_2 & & \text{N:N} & & \text{OH} \\ & \longrightarrow & & \xrightarrow{+\text{H}_2\text{O}} & \quad + \text{N}_2 \\ \text{SO}_3\text{H} & & \text{SO}_3^- & & \text{SO}_3\text{H} \end{array}$$
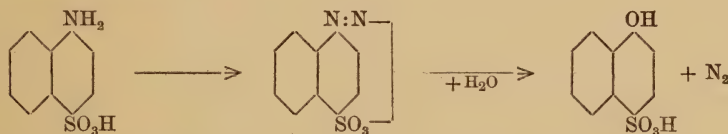
With this strength of sulphuric acid solution, coupling always takes place to some extent between the, as yet, unchanged diazo compound and the naphthol sulphonic acid formed, yielding a red azo dyestuff.   This could be prevented by using a stronger acid solution, but in that case another side reaction is favoured—namely, elimination of the sulphonic acid group by hydrolysis.   The method is not now used.

NW-acid has also been made by heating sodium naphthionate with 50 per cent. caustic soda solution in an autoclave at 240° to 260° (G.P. 46307).   But poor yields are obtained by this process.   The reaction has been investigated by Fierz-David (*Helv. Chim. Acta*, 1920, **3,** 318), who found that, besides NW-acid, a large proportion of α-naphthol and traces of 1 : 4-dihydroxynaphthalene were formed.   The maximum yield of NW-acid obtained was 54 per cent.

The best method of converting naphthionic acid to NW-acid is that discovered by Lepetit in 1896 and patented later by Bayer and Co. in G.P. 109102.   The naphthionic acid is acted on by sodium bisulphite, which quantitatively replaces the amino group by hydroxyl.   This reaction was independently discovered by Bucherer, who extended its application to similar compounds and also to the reverse process of the amidation of hydroxyl compounds.   It is generally known as the Bucherer reaction, and has proved exceedingly useful in the preparation of many amines and phenols of the naphthalene and benzene series (see p. 139 for further details of this reaction).

The preparation is carried out as follows : 32 kg. of sodium naphthionate is heated

under reflux with 20 litres of water and 75 kg. of sodium bisulphite (40° Bé—*i.e.*, 40 per cent.) for twenty-four hours. The liquid is then acidified with hydrochloric acid. This precipitates any unchanged naphthionic acid, which is filtered off. The excess of bisulphite is also decomposed, sulphur dioxide being evolved. The intermediate sulphite derivative of the naphtholsulphonic acid is only slowly hydrolysed by acid, but is quickly attacked by alkali. The liquid is now made alkaline with caustic soda and boiled for a short time to hydrolyse the sulphite derivative and to expel ammonia. On making acid again, the naphtholsulphonic acid is set free and the sulphite formed in the hydrolysis is decomposed, more sulphur dioxide being evolved. The solution of NW-acid so obtained may be used direct for the preparation of dyestuffs, or the sodium salt may be salted out in the usual way.

NW-acid is used as an end component for azo dyes. Coupling with diazo compounds takes place (in alkaline solution) in the ortho position to the hydroxyl group. It is used particularly in conjunction with diazotised aminoazobenzene and aminoazotoluene to produce the Cloth Reds, and with diazotised diamines of the benzidine series for direct cotton colours of blue shades.

1 : 5- **and** 1 : 8-**Dinitronaphthalenes :**
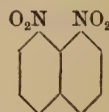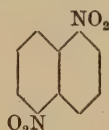
1 : 5-**Dinitronaphthalene** crystallises in yellow needles from glacial acetic acid, m.p. 216°. Insoluble in water, scarcely soluble in concentrated sulphuric acid and cold nitric acid, as also in most organic solvents. In benzene it is sparingly soluble in the cold, but easily soluble when hot. In the ordinary technical pyridine 1 part dissolves in 125 parts cold, and in 10 parts hot.

1 : 8-**Dinitronaphthalene** crystallises in yellow rhombic tables, m.p. 172°. It is in general more soluble than the 1 : 5-compound. Concentrated sulphuric acid dissolves it. 1 part is soluble in 10 parts of cold pyridine bases and in 1·5 parts of hot pyridine.

A mixture of these two dinitronaphthalenes is formed, when naphthalene or α-nitronaphthalene is nitrated with the necessary quantity of nitric acid as mixed acid. It has been found best to proceed from α-nitronaphthalene. The nitration is described by Friedländer (*Ber.*, 1899, **32**, 3531) as follows:

α-Nitronaphthalene is dissolved in four to five times its weight of concentrated sulphuric acid and nitrated at 0° with the calculated quantity of nitric acid as a mixture of 1 part of nitric acid (D 1·4) with 2 parts of sulphuric acid. A red solution is at first formed, but, owing to separation of the nitro compounds, this soon becomes white and thick. When the nitration is finished, the mixed dinitro compounds are isolated as usual by dilution with water, filtration, and washing. The mixture is used in the preparation of Naphthazarin and a few sulphur colours.

For certain dyes, however, the individual dinitro compounds are required, and several different methods have been used for their separation, methods which depend

on their difference in solubility.   For example, the dry mixture is boiled with acetone, which dissolves out the 1 : 8-compound, and the extractions are continued until the melting-point of the residue rises to 212°.   Another and quicker method is to dissolve the whole mixture in six times its weight of boiling pyridine bases.   On cooling, the 1 : 5-compound mostly crystallises out, and by concentrating the mother liquor to a third of its volume most of the remainder is obtained.

The nitration may also be so carried out, by using more sulphuric acid than given above, as to give a good separation of the two substances (G.P. 117368).   100 parts of α-nitronaphthalene is dissolved in 600 parts of concentrated sulphuric acid and nitrated as before with a mixture of 51 parts of nitric acid (D 1·4) and 260 parts of sulphuric acid.   When the nitration is finished, the reaction mixture is heated to 80° to 90° until the dinitro compounds have gone into solution.   On cooling, almost all the 1 : 5-compound separates, while the 1 : 8- remains in solution and may be isolated, after filtration, in the usual way.

Another method of separation depends on a remarkable reaction undergone by 1 : 8-dinitronaphthalene when heated with neutral sulphite, the 1 : 5-compound being unattacked (G.P. 215338, 221383, Meister Lucius and Brüning).   When boiled with excess of sodium bisulphite, both dinitronaphthalenes yield sulphonic acid derivatives of the corresponding diamines.   But if heated at 80° to 90° with neutral sulphite, the 1 : 8-compound is attacked and free alkali is developed.   This, if allowed to accumulate, would decompose the dinitronaphthalenes, forming deeply coloured soluble compounds.   But if the alkali is neutralised as formed, or if arrangement is made for its setting free ammonia in the solution, the reaction proceeds smoothly, the 1 : 8-compound only being affected, with formation of 1-naphthylsulphamino-4 : 7-disulphonic acid, a substance which is easily hydrolysed to 1-naphthylamine-4 : 7-disulphonic acid (Dahl's acid III, see p. 150) :
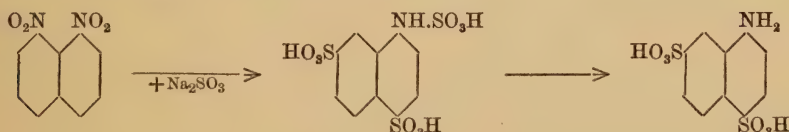
200 kg. of a 60 per cent. paste of the mixed dinitronaphthalenes is heated for five to six hours at 80° to 90° with a solution of sodium ammonium sulphite made from 740 kg. of 40 per cent. bisulphite and 140 kg. of 25 per cent. ammonia.   The unchanged 1 : 5-compound is filtered off.   On cooling the 1-naphthylsulphamino-4 : 7-disulphonic acid crystallises out as needles.   It is hydrolysed by stirring with concentrated hydrochloric acid for several hours, and the 1-naphthylamine-4 : 7-disulphonic acid purified by recrystallising from hot water.

1-**Naphthylamine**-4 : 6- **and** 4 : 7-**disulphonic acids** (Dahl's acids, II and III):
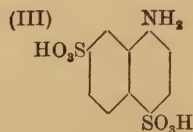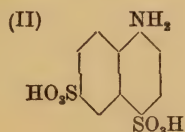
1-**Naphthylamine**-4 : 6-**disulphonic acid** crystallises in needles from hot water, in which it is very soluble, though much less so in cold water.   Solutions of the acid and its salts show blue fluorescence.   The salts are soluble in water.   The calcium salt crystallises in needles with $5H_2O$ and is soluble in 85 per cent. alcohol, but insoluble in 96 per cent. alcohol.

1-**Naphthylamine**-4 : 7-**disulphonic acid** crystallises in needles from water, in which it is only sparingly soluble.   100 parts of water at 20° dissolve 0·7 part of the acid, and at 100° 5 parts.   The sodium and potassium salts are readily soluble in water, the acid sodium salt much less soluble, and the barium and calcium salts sparingly soluble. The calcium salt is insoluble in 85 per cent. alcohol.   Solutions of the acid and its salts show blue fluorescence.

A mixture of the two acids, in the proportion of 30 per cent. of II to 70 per cent. of III, is formed when naphthionic acid is sulphonated at 30° with three and a half times its weight of 25 per cent. oleum (G.P. 41957, Dahl and Co.).   About three days are required to complete the sulphonation.   The acids are then converted into calcium salts in the usual way and evaporated to dryness.   The finely powdered mixture is extracted with ten times its weight of 85 per cent. alcohol, which dissolves out the 4 : 6-salt.   The separated calcium salts are then converted into sodium salts.

1-Naphthylamine-4 : 7-disulphonic acid may also be obtained alone from 1 : 8-dinitronaphthalene (p. 149).

The two acids are used, generally in mixture, as first components in a few black disazo dyes, in which they are coupled with α-naphthylamine as middle component. They are also used in one dye, Apollo Red, or Archil Substitute, as end components.

CHAPTER X

NAPHTHALENEMONOSULPHONIC ACIDS AND THEIR DERIVATIVES

The monosulphonation of naphthalene has been studied by Merz and Weith (*Ber.*, 1870, **3**, 195), Euwes (*Rec. trav. chim.*, 1909, **28**, 298), and by Fierz-David and Weissenbach (*Helv. Chim. Acta*, 1920, **3**, 312). Their results show that in general a mixture of the α- and β-sulphonic acids is formed, in which the proportions of the two acids vary with the temperature of sulphonation, the proportion of α-acid being high at temperatures under 80° and decreasing with rise of temperature to a minimum of 15 per cent. at 160°. Euwes has also shown that either acid can be transformed into the other by heating in sulphuric acid, so that at a definite temperature a mixture in definite proportions of the two acids is obtained. Some idea of the composition of such equilibrium mixtures may be obtained from the following table given by Euwes from the results of heating naphthalene and 100 per cent. sulphuric acid in equimolecular ratio at various temperatures for eight hours :

Temperature.	Naphthalene Recovered (per Cent.).	Percentages in Product of—		Sulphone.
		α-Acid.	β-Acid.	
80°	27·0	96·4	3·6	—
100°	20·0	83·2	16·8	—
129°	10·0	44·4	55·6	1·0
138·5°	8·6	28·4	71·6	—
150°	6·4	18·3	81·7	3·2

At temperatures under 40°, even with a large excess of sulphuric acid, some naphthalene escapes sulphonation.

It is stated in G.P. 50411 (Chemische Fabrik Grünau, Landshoff, and Meyer) that naphthalene, sulphonated with 93 per cent. sulphuric acid at 40°, gives the α-acid as the sole product. This has been disproved by Fierz-David and Weissenbach, who showed that under all conditions a mixture of α- and β-acids is obtained. Even when sulphonation is carried out below 0°, about 2 per cent. of the sulphonation product is β-acid.

Naphthalene-α-sulphonic acid :
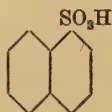
The acid crystallises with $2H_2O$, m.p. 90°. It is soluble in water and alcohol, but is sparingly soluble in slightly diluted sulphuric acid. It is rather easily hydrolysed on heating with dilute sulphuric acid at 160°.

The sodium salt crystallises with $\frac{1}{2}H_2O$.

The potassium salt ($+\frac{1}{2}H_2O$) dissolves in 13 parts of water at 11°.

The calcium salt ($+2H_2O$) dissolves in 16·5 parts of water at 11°, and dissolves calcium sulphate easily.

The barium salt ($+H_2O$) dissolves in 87 parts of water at 11°.

The aniline salt crystallises in white leaflets, m.p. 183°.

The chloride melts at 68°.

The preparation of the pure acid is described by Fierz-David and Weissenbach (*loc. cit.*), but the conditions used are not such as would normally be employed.

If the sodium salt is to be isolated for subsequent fusion to α-naphthol or for other purposes, the following method is suitable (Ullmann, "Enzyklopädie," vol. **8**, p. 319):

150 to 200 parts of 93 per cent. sulphuric acid is warmed to 40° and 100 parts of finely powdered naphthalene stirred in. Stirring is continued until the naphthalene has completely dissolved. The sulphonic acid separates in liquid form, and either care must be taken that no solid sulphonic acid from a previous operation is present (in which case the mass would suddenly go solid and stirring would be impossible), or the mixture is impregnated with a little solid sulphonic acid at the start, when crystallisation takes place gradually and a stirrable crystalline product is obtained. The mixture is now diluted with water, unchanged naphthalene filtered off, converted by milk of lime into the calcium salt, and this into the sodium salt in the usual way, the solution of the sodium salt being evaporated to dryness.

The chief use to which the α-sulphonic acid is put is its nitration to a mixture of the 1 : 8- and 1 : 5-nitronaphthalenesulphonic acids, and for this purpose the acid need not be isolated. Moreover, a sufficiently large excess of stronger sulphuric acid is used to obtain complete sulphonation, and to assist in the subsequent nitration. In this case, then, the sulphonation is carried out as follows (Fierz-David, " Farbenchemie," 1920, p. 36):

128 gms. of finely powdered naphthalene is rapidly stirred into 260 gms. of monohydrate at 0°. As soon as the naphthalene is all added, the mixture is impregnated as before with a little solid α-sulphonic acid in order to prevent sudden solidification to a hard mass. Sulphonation begins at once with evolution of heat, and the temperature rises to about 35°. If the naphthalene is not completely sulphonated at this temperature, the mixture is heated further, to 60° at the highest, until all the naphthalene is sulphonated. The mixture so obtained is then nitrated, as described later (p. 154).

α-Naphthol is obtained by fusion of naphthalene-α-sulphonic acid with caustic soda at 270° to 320°, the method used being the same as that described under β-naphthol.

The α-naphthol obtained from the sulphonate, however, always contains some β-naphthol, and the method of preparation from α-naphthylamine (p. 145) is generally preferred.

1-Naphthylamine-8-**sulphonic acid** (Peri-acid)—

HO₃S NH₂

CHART VIII.—NAPHTHALENEMONOSULPHONIC ACIDS AND THEIR DERIVATIVES.
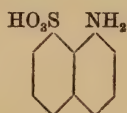
—and 1-**Naphthylamine**-5-**sulphonic acid** (Laurent's acid) :
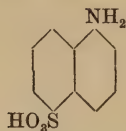
Peri-acid crystallises in needles with $1H_2O$, very sparingly soluble in water. 1 part of the acid dissolves in 4,000 parts of water at 21° and in 238 parts at 100°.

The sodium and potassium salts are sparingly soluble in water. 100 parts of water at 24° dissolve 1·13 parts, and at 100° 2·67 parts of the sodium salt.

Laurent's acid forms microscopic needles with $1H_2O$. 1 part of the acid dissolves in 950 parts of water at 15°, but in hot water the acid is moderately soluble.

The salts are soluble in water. Their solutions show a greenish fluorescence. Addition of bromine water produces an intense violet colouration, changing quickly to red-violet, and finally disappearing.

These two acids are obtained together by reducing the mixture of the corresponding nitrosulphonic acids which is formed when naphthalene-α-sulphonic acid is nitrated.

128 gms. of naphthalene is sulphonated, as described on p. 152. When sulphonation is finished, the mixture is cooled to 10° to 15° and 103 gms. of 60 per cent. nitric acid slowly added over two and a half hours, the temperature being maintained at 10° to 15°. The thick crystalline mass of sulphonic acid dissolves up as the nitrosulphonic acids form. The solution is then stirred for a further twelve hours to complete nitration, and poured into 2 litres of water. A solution is thus obtained containing 1 : 8- and 1 : 5-nitronaphthalenesulphonic acids in the ratio 2 : 1, together with less than 5 per cent. of the nitrosulphonic acids (1 : 6- and 1 : 7-) formed from the β-naphthalenesulphonic acid present in the sulphonation mixture.

The nitro-acids are now reduced by adding the solution with vigorous stirring to 260 gms. of iron turnings, the addition being made at such a rate that the solution in the reduction vessel remains neutral to Congo paper. Much heat is developed, and the temperature rises to about 80°. The solution becomes violet in colour owing to formation of intermediate hydroxylamine compounds. After the solution of nitro-acids has all been added, the mixture is heated to boiling until the violet colour changes to greenish, which indicates completed reduction. The 1: 5- and 1 : 8-aminoacids may now conveniently be separated as their sparingly soluble ferrous salts. For this purpose 40 gms. of iron powder is added cautiously to the still boiling solution, when the ferrous salts separate as grey-white crystals. After cooling, sulphuric acid is added till the mixture is definitely mineral acid, which decomposes the ferrous salts, precipitating the free amino-acids. These are filtered off, well washed to remove ferrous sulphate, and then dissolved in sufficient water, together with 40 gms. of magnesite. The solution is filtered and, on adding salt till a 10 per cent. salt solution is formed, the 1 : 8-salt separates, and after some time is filtered off. On acidifying the filtrate the 1 : 5-acid is precipitated.

The yield is about 100 gms. of 100 per cent. 1 : 8-acid and 40 gms. of 100 per cent. 1 : 5-acid. The acids are estimated by titration with standard nitrite solution.

The above method of reduction of the nitro-acids is not generally applicable to the nitronaphthalenesulphonic acids, as often the reduction under these conditions will not proceed beyond the hydroxylamine stage. This is the case with the 1 : 6- and 1 : 7-nitro-acids present as impurities in the above case, and the method, therefore, serves very well for removal of the reduction products of these acids from the final product, since the hydroxylamino-acids are soluble and are, therefore, washed away with the ferrous sulphate.

Another reduction process, which is generally applicable, is carried out by first neutralising the diluted solution of nitrosulphonic acids with chalk (or partly with magnesite, so as to form the magnesium salts), filtering off calcium sulphate, making the filtrate faintly acid again, and running the solution into a boiling mixture of water and iron borings previously etched by a little acetic acid. The process is more fully described on p. 163. The 1 : 6-and 1 : 7-nitro-acids in this case are completely reduced to the amino-acids (Cleve's acids), which then appear as impurities, especially in the Laurent's acid.

Peri-acid is worthless as a dyestuff intermediate, either when used as a first or as an end component in azo dyes. But a number of useful derivatives are obtained from it, and these will be described later.

Laurent's acid, on the other hand, is employed, both as first and as end component, in several commercial dyestuffs. When used as end component, coupling takes place in the *ortho* position to the amino group.

1-**Phenylnaphthylamine**-8-**sulphonic acid** (Phenylperi-acid) :

$$HO_3S \quad NH.C_6H_5$$
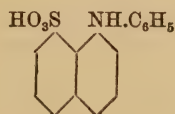
The acid crystallises in leaflets, sparingly soluble in water. The sodium salt is easily soluble.

Several patents (G.P. 70349, 118655, 170630) describe the preparation of this substance by heating Peri-acid with aniline in an autoclave at 140° to 170° under various conditions. But the use of an autoclave is unnecessary.

Peri-acid is heated and stirred with three times its weight of aniline. Any water present is first distilled off under reduced pressure. Heating is then continued under ordinary pressure at 160° to 170° for twenty-four hours. The excess of aniline is then distilled off and the aniline salt of Phenylperi-acid, which remains, is converted into the sodium salt by addition of the necessary quantity of caustic soda solution. The aniline set free is distilled off in steam, and the residual solution of the sodium salt of Phenylperi-acid used directly for the preparation of dyestuffs.

p-**Tolylperi-acid** is prepared similarly, using *p*-toluidine in place of aniline.

Phenyl- and tolylperi-acids are used particularly for the preparation of navy blue and black disazo dyes in which they play the part of end components, α-naphthylamine being the middle component in most cases.

Naphthasultone—
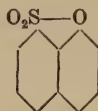
—crystallises from alcohol in prisms, m.p. 154°, almost insoluble in water.

This substance is formed in almost quantitative yield when Peri-acid is diazotised in the usual way with nitrite and dilute sulphuric acid and the suspension of the sparingly soluble diazo compound in the dilute acid is boiled.

It is an anhydride of α-naphthol-8-sulphonic acid, and may be converted into this acid by heating with alcoholic ammonia at 130°, adding lead acetate, and decomposing the lead salt with hydrogen sulphide. This, however, is not usually carried out. Instead it is sulphonated and converted into 1-**naphthol**-4 : 8-**disulphonic acid :**
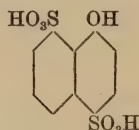
The sulphonation is carried out simply by heating the sultone with two to three times its weight of sulphuric acid at 80° to 90° until the product is soluble in water (G.P. 40571, Schöllkopf Aniline and Chemical Co.). This intermediate is used for azo dyes.

α-**Naphthylamine**-4 : 8-**disulphonic acid :**
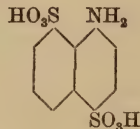
Not much information is available regarding this acid. The monosodium salt crystallises in scales, sparingly soluble in cold water. The disodium salt is easily soluble.

This acid is prepared by sulphonating Peri-acid with three times its weight of 10 per cent. oleum, the two being mixed in the cold, and the sulphonation finished at 100° (G.P. 40571, Schöllkopf). The neutral sodium salt is obtained in the ordinary way by neutralising the diluted melt with lime and addition of soda to the filtered solution of the calcium salt.

α-Naphthylamine-4 : 8-disulphonic acid is not used as a dyestuff intermediate itself, but gives rise to several important intermediates.

1 : 8-**Aminonaphthol**-4-**sulphonic acid** (S-acid) :
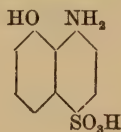
The acid crystallises in needles, almost insoluble in water. The alkali salts are easily soluble, and their solutions show bluish-green fluorescence.

S-acid is prepared by fusion of 1-naphthylamine-4 : 8-disulphonic acid with caustic soda (or, according to Fierz-David, preferably with caustic potash) at 200° in open pans (G.P. 63074, Badische; G.P. 75317, Bayer).

According to the later patent the sodium salt of the naphthylaminedisulphonic acid is heated with 4 to 5 parts of caustic potash and 1 part of water at 200° until the melt becomes mobile and a sample dissolved in water shows the characteristic fluorescence. The melt is then dissolved in twice its weight of water and made just acid with hydrochloric acid, when the S-acid separates.

The use of S-acid as an intermediate for azo dyes is dealt with in connection with other 1 : 8-aminonaphthol-sulphonic acids on p. 172.

1 : 8-**Dihydroxynaphthalene**-4-**sulphonic acid** (Dioxy-S-acid) :
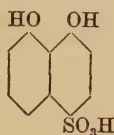
The acid and its salts are soluble in water.

This acid is obtained if the fusion of 1-naphthylamine-4 : 8-disulphonic acid is carried out at a higher temperature (250°) than that used for S-acid (G.P. 71836, Bayer), or it may be obtained from S-acid by fusion with caustic soda at 220° to 250° (G.P. 80315, Bayer).

But these acids are so readily oxidised in alkaline solution at high temperatures, that the following preparation at a much lower temperature, an application of the Bucherer reaction, is probably preferable (G.P. 109102, Bayer).

23·9 kg. of S-acid are stirred with 60 litres of water in an enamelled pan and exactly neutralised with caustic soda. 128 kg. of bisulphite solution (40° Bé—i.e., 38 to 40 per cent.) are added and the solution heated at 90° until a sample on acidifying gives only a slight precipitate of unchanged S-acid. The solution is then acidified, unchanged S-acid filtered off, made alkaline with caustic soda, and boiled till all the ammonia is expelled. It is then acidified with hydrochloric acid and again boiled to expel sulphur dioxide. The neutralised solution can then be used direct, or the substance may be salted out.

Dioxy-S-acid is used as an end component in azo dyes, and in consequence of its hydroxyl groups imparts to them the property of forming chromium lakes by after-chroming, with consequent increase of intensity and fastness.

1 : 8-**Naphthasultam**-2 : 4-**disulphonic acid** :
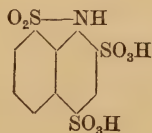
This acid forms a disodium salt which crystallises in fine needles with $2H_2O$, soluble in water without fluorescence. A trisodium salt is also formed, which crystallises in yellow leaflets soluble in water with green fluorescence, similar to that of fluorescein.

The 1-naphthylamine-2 : 4 : 8-trisulphonic acid, of which this substance is the anhydride, is unknown.

The sultam-disulphonic acid is prepared by adding 300 parts of the acid sodium salt of 1-naphthylamine-4 : 8-disulphonic acid gradually to 600 parts of 40 per cent. oleum. The solution is then warmed to 80° to 90°, at which it soon sets to a solid white mass. Heating is continued until a sample, diluted with water, no longer diazotises or couples with diazotised aniline (after reducing the acidity of the test solution with sodium acetate). The mixture is then diluted with ice-water and the acid converted through the calcium salt into the sodium salt in the usual way, the solution of sodium salt being evaporated to dryness, in preparation for the fusion with alkali, by which it is converted into the aminonaphtholsulphonic acid (see later).

The sodium salt may be prepared in pure crystalline form by adding alcohol to a hot concentrated solution of it and cooling, when the salt separates almost completely in lustrous large yellow leaflets.

Naphthasultamdisulphonic acid is not used as a dyestuff intermediate, but is fused with alkali to produce 1 : 8-aminonaphthol-2 : 4-disulphonic acid (2S-acid):
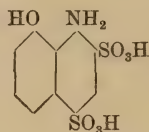
The acid is readily soluble in water. The acid sodium salt crystallises in fine needles, easily soluble in water, but precipitated from solution by addition of hydrochloric acid. Dilute solutions of the alkali salts show a beautiful green fluorescence. 2S-acid gives a reddish-yellow soluble diazo compound which can be salted out of solution.

The preparation, as also that of the previously described naphthasultamdisulphonic acid, is given in G.P. 80668 (Bayer; *cf.* also Dressel and Kothe, *Ber.*, 1894, **27**, 2139).

1 part of the sodium salt of the naphthasultamdisulphonic acid is fused with $2\frac{1}{2}$ parts of caustic potash or soda, to which 0·2 part of water has been added, in an open pan at 170°. (The reaction may also be carried out, using more water, in an autoclave.) As soon as a sample of the melt, dissolved in water and coupled with a diazo compound, shows no increase in dye formation, the whole melt is dissolved in water and the solution acidified with hydrochloric acid. The acid sodium salt of 2S-acid separates in colourless needles. It may be purified by recrystallisation from water.

The use of 2S-acid as an intermediate for azo dyes is considered later (p. 172) in connection with other 1 : 8-aminonaphtholsulphonic acids.

1-**Amino**-5-**naphthol**—
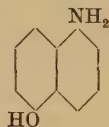
—may be prepared from 1-naphthylamine-5-sulphonic acid (Laurent's acid) by heating the Laurent's acid with 5 molecular proportions of caustic soda as 30 per

cent. solution in an autoclave (rotary or stirred) at 250° for three hours. As by-products 1 : 5-dihydroxynaphthalene and α-naphthylamine are also formed. The melt is worked up by filtering off the sodium salt of any unchanged Laurent's acid (this being insoluble in the caustic soda solution). The naphthylamine is then extracted with ether. On saturating the alkaline solution with carbon dioxide, the aminonaphthol is precipitated in 52 per cent. yield (Fierz-David, *Helv. Chim. Acta,* 1920, **3,** 318).

1 : 5-**Dihydroxynaphthalene :**
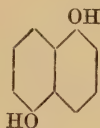
Laurent's acid may also be used as a source of this important intermediate (Fierz-David, *loc. cit.*). The preparation is carried out, as given above, for 1 : 5-amino-naphthol, except that the reaction mixture is heated at 290° for three hours. The higher temperature favours production of the dihydroxy compound at the expense of the aminonaphthol. After removing unchanged Laurent's acid, α-naphthylamine and aminonaphthol as given above, on making the solution acid with hydrochloric acid, 1 : 5-dihydroxynaphthalene is precipitated. The yield under these conditions is 60 per cent.

Another method of preparation is given on p. 178.

Naphthalene-β-sulphonic acid :

The anhydrous acid melts at 90·5° to 91°, and is easily soluble in benzene and toluene. It forms a trihydrate, crystallising in leaflets, m.p. 83°, very soluble in water. The trihydrate loses water in the desiccator, giving a monohydrate, m.p. 124°. The chloride melts at 79°, the amide at 212°.

The sodium salt (anhydrous) dissolves in 17 parts of water at 25°, the calcium salt (also anhydrous) in 76 parts of water at 10°, the barium salt ($+H_2O$) in 290 parts of water at 10°.

The aniline salt forms white needles, m.p. 269°, soluble in alcohol.

The sulphonation of naphthalene to the β-acid has been studied by Witt (*Ber.,* 1915, **48,** 743), who gives much exact information regarding it. His method of preparing the substance is convenient and quick, therefore suitable for laboratory purposes. 250 gms. of naphthalene is melted and heated to 160°. 400 gms. of sulphuric acid (93·7 per cent.) is stirred in, the temperature being maintained about 160°. This requires about fifteen minutes. Sulphonation is very rapid, and after a further five minutes is complete. After standing for a short time, the solution is poured into 300 c.c. of water. On cooling, nearly all the β-acid crystallises out as trihydrate, being salted out by the α-acid present. (As already mentioned, sulphonation of naphthalene at 160° gives a mixture of 85 per cent. of β-acid with 15 per cent. of α-acid.) The β-acid may be purified (from a little sulphone) by dissolving 600 gms.

of it in 300 c.c. of water at 70°, adding 100 c.c. of concentrated hydrochloric acid, and allowing to cool. It crystallises from this solution as trihydrate.

It is possible, however, to sulphonate naphthalene completely with a much smaller excess of acid than that used by Witt, and on the large scale, especially where the β-sulphonic acid is to be converted into β-naphthol (its principal use), a weight of sulphuric acid equal to that of the naphthalene is found to suffice, and to give most economical working.

A detailed description of the manufacture of β-naphthol is given by R. N. Shreve (*Colour Trade Journal*, 1924, **14**, 43), of which the following are the essential features:

(*a*) **Naphthalene β-sulphonic Acid.**—Naphthalene (3,350 lbs.) is heated till melted, and at 90° to 100° C. sulphuric acid (3,350 lbs. of 93 per cent.) is run in while stirring. The temperature is allowed to rise to 160°, and is kept there until all the acid has been added. Heating is then continued at 160° to 165° for several hours until the sulphonation is finished. During this time the water produced by the reaction, together with some naphthalene, distils off and passes through condensers surrounded by water at 90°, to prevent blocking by solid naphthalene.

The next stage of the process consists in the removal of the α-sulphonic acid by taking advantage of its comparative ease of hydrolysis in diluted acid at 160°. Sulphonation being complete, dry steam is blown into the solution, which is kept at 160°, when the α-sulphonic acid is hydrolysed to naphthalene and sulphuric acid, the naphthalene distilling off through the condensers. About 18 per cent. of the naphthalene used is recovered in this operation and in the distillate during sulphonation. Dry steam must be used or foaming takes place. About seven hours' passage of steam is required to reduce the α-sulphonic acid content to 0·15 to 0·20 per cent.

The sulphonation mixture is now run into 13,400 lbs. of water with vigorous stirring, and a solution of 4,750 lbs. of salt in 9,350 lbs. of water added, which salts out the sodium salt of the β-sulphonic acid fairly completely after stirring for ten hours and allowing to cool to 25° to 30°.

In this connection some figures are given by W. T. Cooke (*J. Soc. Chem. Ind.*, 1921, **40**, 56T, 239T), showing the influence of sodium chloride and sodium sulphate on the solubility of sodium β-naphthalenesulphonate. He shows that the solubility of the β-salt is reduced practically to zero when the concentration of NaCl or Na_2SO_4 reaches about 10 gms. in 100 gms. of solution, especially at lower temperatures (about 30°). The concentration of NaCl + Na_2SO_4 obtained, using the above quantities, is about 12 to 14 parts per 100 parts of solution.

The β-salt is now filtered off and pressed, by which means the water content of the press-cake is reduced to about 30 per cent. This is sufficiently low for the subsequent fusion.

(*b*) **Fusion to β-Naphthol.**—1,975 lbs. of caustic soda (95 per cent.) and 400 lbs. of water are melted together in the fusion pot, and heated, whilst stirring, to 305°. β-salt, in the form of the ground press-cake containing 30 per cent. of water, is then added until the temperature falls to 295°, when the addition is stopped until the temperature again rises to 305°, then more sulphonate is added, and so on, until the full charge of 6,540 lbs. of moist β-salt has been added. The melt is then kept at 300° for

six hours.   The finished melt is run into 2,500 gallons of water, using for this purpose the weak β-naphthol washings from a previous operation.   The hot solution is filtered at 80° and dilute sulphuric acid added to the filtrate till it is no longer alkaline to phenolphthaleïn. β-Naphthol separates in part as solid, and the whole is liquefied by heating to 95°, when, on allowing to settle, the β-naphthol forms the upper layer. The sulphite liquor beneath is run off and cooled, when about 10 per cent. of the β-naphthol separates and is removed.   The liquid β-naphthol is washed with boiling hot water until the wash water shows a specific gravity of 1. The naphthol is then dried at 115°, and distilled in a vacuum.   Under a pressure of 50 mm. it distils at 185° to 190°.

The yield of sulphonate from naphthalene is 86 per cent., and of pure β-naphthol from sulphonate 74 per cent.   The overall yield of pure naphthol from naphthalene is, therefore, about 64 per cent.

There is a considerable residue in the vacuum still, which forms when cold a black shiny brittle mass known as naphthol pitch and used as insulating material in electric cables.   It probably contains $\beta\beta'$-dinaphthol or $\beta\beta'$-dinaphthylene oxide.

β-**Naphthol**—
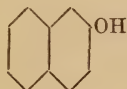
—crystallises in lustrous scales, m.p. 122°, b.p. 285° to 286°, D^4 1·217.   It is almost insoluble in cold water, but dissolves in 75 parts of boiling water.   It is soluble in most organic solvents, and in solutions of caustic alkalies, but not carbonates.   It sublimes easily.   It is only slightly volatile in steam at 100°, but may be distilled in superheated steam.

The commercial product usually shows a very high degree of purity (over 99 per cent.).   It is estimated by titration with standard iodine solution ($3I_2$ used per molecule of naphthol), or with diazotised p-nitraniline, the naphthol being dissolved in the least possible caustic soda and carbonate added as required.

β-naphthol is used, as a dyestuff intermediate, for azo dyes, chiefly of the monoazo class.   Coupling with diazo compounds takes place in the α-position ortho to the hydroxyl group :

R.N : N.Cl   +   —OH $\longrightarrow$ R.N : N—   HO
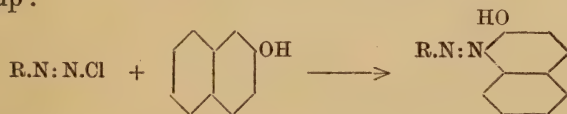
Its chief use is for the production of Para Red dyeings on the fibre by coupling with diazotised p-nitraniline.   The monoazo dyestuffs, of which Para Red is a type, in which nitro-, chloro-, nitrochloroanilines and similar bases containing negative substituent groups figure as first components, are remarkably insoluble bodies, being insoluble in caustic alkalies, notwithstanding the presence of the hydroxyl group. They are specially useful, on this account and also because of their brightness of shade, as lake pigments.

β-Naphthol is also used as an end component in a considerable number of dis- and trisazo dyes.

11

An oxazine dye, Meldola's Blue, is made from β-naphthol by condensation with p-nitrosodimethylaniline.

1-**Naphthylamine**-6-**and** 7-**sulphonic acids** (Cleve's acids):
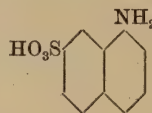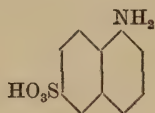
1-**Naphthylamine**-6-**sulphonic acid** crystallises in cubes from hot water, or in leaflets if crystallisation is slow. 1 part dissolves in 1,000 parts of water at 16°. The sodium salt forms two crystalline hydrates with H_2O and $4\frac{1}{2}H_2O$ respectively. It is easily soluble in water, but is readily salted out. The calcium salt is easily, but the barium salt sparingly, soluble in water. The aqueous solutions give with ferric chloride a cornflower blue colouration.

1-**Naphthylamine**-7-**sulphonic acid** crystallises in needles or flat prisms with $1H_2O$. 1 part dissolves in 220 parts of water at 25°. The sodium salt (needles, $+\frac{1}{2}H_2O$) is easily soluble in water, but, unlike the 1 : 6-acid, is not readily salted out. The calcium salt is easily, but the barium salt sparingly, soluble in water. With ferric chloride a blue colouration is obtained, which changes to red with acetic acid.

When naphthalene-β-sulphonic acid is nitrated, a mixture of about equal quantities of 1 : 6- and 1 : 7-nitronaphthalenesulphonic acids is formed, together with a little of the 1 : 3-acid. On reduction these yield the two Cleve's acids.

The usual practice in such preparations is to start from naphthalene and to carry out the whole preparation—sulphonation, nitration, and reduction—without isolation of the intermediate products, as already described in the case of Peri-acid and Laurent's acid (p. 154). A process on these lines is described by Fierz-David (" Farbenchemie," 1920, p. 30). But although such a method is suitable in the case of Peri- and Laurent's acids, prepared from the α-sulphonic acid containing only 4 to 5 per cent. of the β-sulphonic acid, in the present case the proportion of isomers seems too great. When naphthalene is sulphonated so as to produce the maximum proportion of β-acid, the product contains at least 15 per cent. of the α-acid, which on nitration and reduction yield the 1 : 5- and 1 : 8-amino acids (Peri- and Laurent's acids), which are similar in properties to the Cleve's acids and not readily separated from them. For the preparation of fairly pure Cleve's acids, it is advisable, either to isolate the β-sulphonic acid (as sodium salt, see the manufacture of β-naphthol, p. 160), or, without isolating, to hydrolyse the α-sulphonic acid in the mixture with steam at 160°, and then, after cooling, to add the excess of sulphuric acid required to assist in the nitration. The disadvantage of isolating the β-sulphonate is the large excess of sulphuric acid required to redissolve it. In a Cassella patent (G.P. 67017) describing the preparation of these acids, the β-sulphonate is dissolved in five times its weight of sulphuric acid at 30° (a higher temperature must not be used, or β-acid is partly transformed to α-acid). On the other hand, if naphthalene has been sulphonated with about an equal weight of 93 per cent. sulphuric acid and the α-acid has been removed by hydrolysis, on cooling to the low temperature necessary for the nitration, the melt sets to a solid

mass. This difficulty is overcome by adding, at the lowest possible temperature before solidification takes place, such a quantity of 85 per cent. sulphuric acid as will result in a stirrable mixture. The additional quantity of sulphuric acid required for this purpose is about twice that used for the sulphonation. Nitration may be commenced at about 55°, in order to assist in liquefying the mixture, but is continued at 10° to 15°. Nitration at higher temperatures leads to formation of β-nitro derivatives. The calculated quantity of 60 per cent. nitric acid is used. After the nitric acid has been added the mixture is allowed to stand several hours to complete nitration. The solution is then poured into water.

The reduction of the nitrosulphonic acids cannot be carried out in this case in the strongly acid solution, as shown by Fierz-David and Weissenbach (*Helv. Chim. Acta*, 1920, **3,** 305), since in acid solution reduction proceeds only to the hydroxylamine stage. Reduction of a nearly neutral solution of the calcium or, preferably, the magnesium salts with iron borings gives fairly satisfactory results. The process, then, is as follows:

Sufficient magnesite is added to the solution to form the magnesium salts of the nitrosulphonic acids, and neutralisation is completed with chalk or limestone. Calcium sulphate is filtered off, well washed, and the united filtrates, acidified slightly with dilute sulphuric acid, added gradually to a boiling mixture of water and cast-iron borings previously etched with a little acetic acid. For each 128 parts of naphthalene used, about 300 parts of iron, 500 parts of water, and 20 parts of 40 per cent. acetic acid are required for the reduction. When the reduction mixture has become colourless, it is made faintly alkaline to litmus by addition of magnesite, and filtered. From the filtrate, the sodium salt of the 1 : 7-naphthylaminesulphonic acid can be salted out by adding sufficient salt to give a 6 per cent. solution. After stirring for about a day, the 1 : 7-salt is filtered off, and the 1 : 6-acid precipitated from the filtrate by acidifying with hydrochloric or sulphuric acid.

The yields obtained from 128 parts of naphthalene are about 70 parts of the 1 : 7-acid and 80 parts of 1 : 6-acid, as estimated by titration with standard nitrite solution.

For most purposes, the two acids are not separated, as they yield dyes of the same shade and dyeing strength.

The Cleve acids are used, like α-naphthylamine, as middle or end components in various dis- and trisazo dyes, which are navy blue or black in shade. The 6-sulphonic acid is specially used for a few trisazo dyes, of which Benzo Fast Blue FR is typical, this dye being composed as follows :

Aniline ———⟶ Cleve's acid ———⟶ Cleve's acid ———⟶ J-acid.
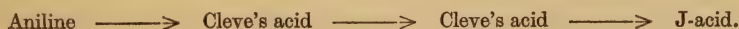
NAPHTHALENEDISULPHONIC ACIDS AND THEIR DERIVATIVES

THE formation of the four disulphonic acids, 1 : 5-, 1 : 6-, 2 : 7-, and 2 : 6-, from naphthalene has already been discussed (p. 136).   It was indicated that low temperature sulphonation yielded a mixture of the 1 : 5- and 1 : 6-acids, while at temperatures above 140° the product was chiefly a mixture of 2 : 7- and 2 : 6-acids.

While uses have not been found for the 2 : 6-acid, the other three form the sources of naphthylamine-, naphthol-, and aminonaphtholsulphonic acids.   For this purpose the disulphonic acids are treated in three different ways :

(i.) By further sulphonation to trisulphonic acids, nitration of these, and reduction, they produce naphthylaminetrisulphonic acids, and these may further be fused with alkali to form aminonaphtholsulphonic acids.

(ii.) By direct nitration and reduction they yield naphthylaminedisulphonic acids, and from these, by replacement of the amino group, naphtholdisulphonic acids.

(iii.) By alkali fusion of salts of the disulphonic acids naphtholmonosulphonic acids and dihydroxynaphthalenes are obtained.

Only for the third of these processes—*i.e.*, for the alkali fusion, need the disulphonic acids be isolated.   They are generally made by sulphonation of naphthalene, or sometimes of the monosulphonic acids, and further sulphonated or nitrated without isolation.

Naphthalene-1 : 5-**disulphonic acid :**
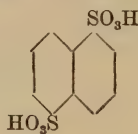
The acid crystallises in lustrous scales, with $4H_2O$, very soluble in water.   The anhydrous acid melts at 240° to 245° with decomposition.   The disodium salt (scales, $+2H_2O$) dissolves in 9 parts of water at 18°.   The barium salt is described by Armstrong and Wynne as crystallising with $4H_2O$ and as easily soluble in water, but Fierz-David and Hasler (*Helv. Chim. Acta*, 1923, **6**, 1133) state that it crystallises with $1H_2O$, and is almost insoluble.   However, the inconsistency may be only apparent, since Fierz-David formed the barium salt from boiling solutions, in which the tetrahydrate is probably not the stable form.

The 1 : 5-acid can be prepared with no simultaneous formation of isomers, according to Armstrong and Wynne (*Proc. Chem. Soc.*, 1886, **2**, 231), by sulphonating naphthalene with chlorsulphonic acid.   Naphthalene is dissolved in carbon disulphide, and a slight excess over two molecular proportions of chlorsulphonic acid added.   When sulphonation is finished, the carbon disulphide is distilled off.   A little of the α-monosulphonic acid is present in the product.   This may be removed by neutralising the solution of the product with lead carbonate, and isolating the lead salts.   These are dried, powdered finely, and extracted with hot alcohol, which removes the lead
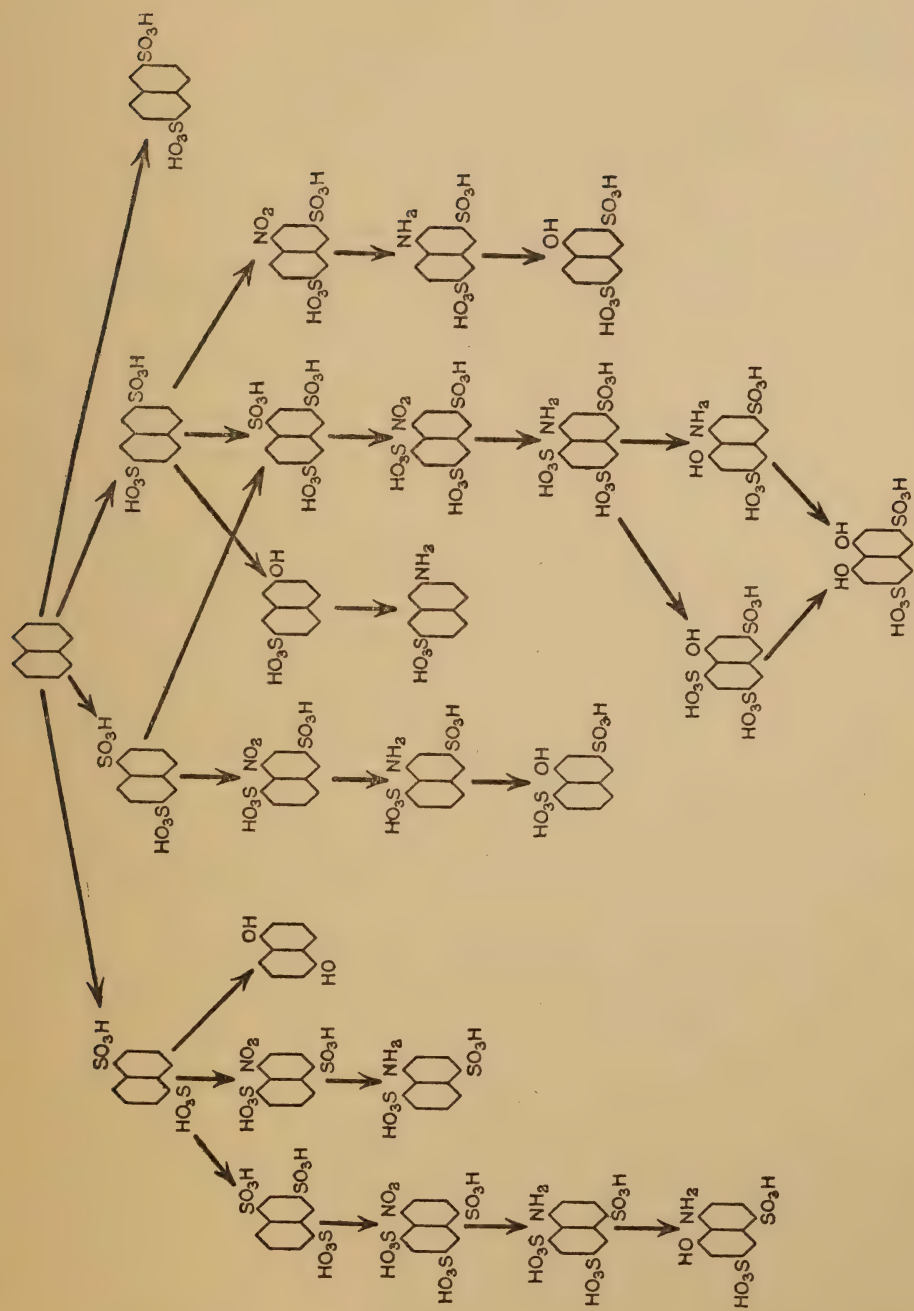
CHART IX.—NAPHTHALENEDISULPHONIC ACIDS AND THEIR DERIVATIVES.

α-sulphonate. The undissolved residue is the disulphonate, from which the acid may be obtained in the usual way.

When formed by sulphonation of naphthalene with oleum, it is always accompanied by the 1 : 6-acid, and its separation from this isomer is best accomplished, according to Fierz-David and Hasler (*loc. cit.*), through the insoluble barium salt. The preparation is described as follows:

128 gms. of finely powdered naphthalene is added during a quarter of an hour with stirring to 300 gms. of 100 per cent. sulphuric acid. As the mass begins to thicken, 300 gms. of 64 per cent. oleum is dropped in, the temperature being allowed to rise to 30°. The quantity of free SO_3 added is 20 per cent. in excess of that required to unite with the water formed by the sulphonation. This excess is found to be required for complete disulphonation. If less is used, it is found that the β-sulphonic acid present is left unchanged. On the other hand, if much more is used, trisulphonic acids are formed. When all the oleum has been added, the solution is stirred (in a closed vessel) for at least eight hours at 40°. A snow-white milky mass is formed. This is poured into 3 litres of water, and 52·5 gms. of 100 per cent. sodium carbonate added. The solution is heated to boiling, and neutralised with barium carbonate. After filtering hot, it is evaporated down to $1\frac{1}{2}$ litres. Hydrochloric acid is then added till the solution is just acid to Congo paper, and to the boiling solution barium chloride solution is added in small portions until no further precipitate forms. As the barium salt of the 1 : 5-acid precipitates at once as a white sandy precipitate, the end point is easily observed. While still warm the precipitate is filtered off and washed with cold water. A yield of 70 to 72 per cent. is obtained—*i.e.*, 274 to 282 gms. of barium salt, $C_{10}H_6(SO_3)_2Ba+H_2O$. The mother liquor contains the soluble barium salt of the 1 : 6-acid, together with a little 2 : 7-salt.

The 1 : 5-acid may be obtained from the salt by stirring it with water and adding the calculated quantity of dilute sulphuric acid. After warming for half an hour on the water-bath, the barium sulphate is filtered off and the filtrate evaporated to crystallising point.

Various other methods of sulphonation and separation of the 1 : 5-acid are described vaguely in the patents (G.P. 45776, G.P. Anm. E. 2619 of 1889).

Naphthalene-1 : 6-**disulphonic acid** :
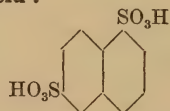
The free acid crystallises with $4H_2O$, and is soluble in water. The disodium salt crystallises with $7H_2O$, 1 part of the salt (calculated as anhydrous) dissolving in 3 parts of water at 18° to 20°. The barium salt ($+3\frac{1}{2}H_2O$) dissolves in 16 parts of water at 18° to 20°.

This acid can be obtained free from isomers by sulphonating the β-monosulphonic acid with chlorsulphonic acid (Armstrong and Wynne, *Proc. Chem. Soc.*, 1886, **2**, 231). The potassium salt of naphthalene-β-sulphonic acid is mixed with three molecular proportions of chlorsulphonic acid, the excess being used in order to obtain a liquid

product. The sulphonation is rapid and is completed by heating on the water-bath for a few minutes. A little sulphochloride is formed. Water is now cautiously added, and the potassium acid sulphate which separates after a time is filtered off, and the filtrate evaporated to dryness.

Fierz-David and Hasler find that the 1 : 6-acid is best obtained by starting from the β-sulphonic acid or by sulphonating naphthalene first at 165°, then at 40°.

128 gms. of naphthalene is heated to 165° and, while stirring, 200 gms. of 100 per cent. sulphuric acid dropped in. After stirring for half an hour at 165°, the solution is cooled to 30°. Then, keeping the temperature below 35°, 275 gms. of 66 per cent. oleum is slowly added during an hour. The solution is stirred for nine hours more at 40°. The quantity of sulphone formed is at most about 0·5 per cent. The solution is now poured into 2 litres of cold water, heated to boiling, and neutralised with barium carbonate. The insoluble barium salt of the 1 : 5-acid precipitates with the barium sulphate. After filtering and washing the residue well, the barium is precipitated from the filtrate by sodium carbonate (about 106 gms.). The barium carbonate having been filtered off, the solution is concentrated to about 500 c.c. On cooling, the sodium salt of the 1 : 6-acid crystallises, and after some hours is filtered off, pressed, and dried. The yield is 140 gms. or about 40 per cent.

If β-sulphonate is used to start with, yields of 55 to 60 per cent. of the 1 : 6-salt can be obtained.

Other methods of preparing the 1 : 6-acid are described in G.P. Anm. B. 9514 of 1889 and G.P. 45229.

Naphthalene-2 : 7-**disulphonic acid :**

The acid crystallises in long deliquescent needles. The disodium salt ($+6H_2O$) and the calcium salt ($+6H_2O$) are easily soluble in water, the barium salt ($+2H_2O$) less soluble.

As already mentioned, this acid, together with the 2 : 6-acid, is formed when naphthalene or its β-sulphonic acid is disulphonated at high temperatures. Above 130°, as shown by Fierz-David, no 1 : 5-acid is present in the sulphonation product, but along with the 2 : 7- and 2 : 6-acids there is always a substantial proportion of 1 : 6-acid. At 160°, when the proportion of 2 : 7-acid is probably a maximum, the composition of the mixture is roughly 65 per cent. of 2 : 7-acid, 10 per cent. of 1 : 6-acid, and 25 per cent. of 2 : 6-acid. The proportion of 2 : 6-acid can be fairly well determined owing to its forming an insoluble barium salt, but the proportions of the 2 : 7- and 1 : 6-acids are not definitely ascertained, as a good method of separation is lacking. The 2 : 6-acid can also be separated from the other two by means of its sparingly soluble calcium and lead salts. The calcium salt of the 2 : 6-acid loses water of crystallisation at 100°, being converted into the almost insoluble anhydrous salt.

The 2 : 7-acid may, therefore, be prepared almost free from 2 : 6-acid but still

containing some 1 : 6-acid by the method of Ebert and Merz (*Ber.*, 1876, **9**, 592). Naphthalene is sulphonated with five times its weight of sulphuric acid at 160° for five hours. The product is poured into water and converted into calcium salts. Ebert and Merz evaporated the solution of calcium salts to dryness and heated at 200° to 230° until dehydrated, when on extraction with water, the 2 : 6-salt remained undissolved. But evaporation to dryness is not necessary. The solution of calcium salts from 200 kg. of naphthalene and 1,000 kg. of sulphuric acid, after evaporating to a volume of 3 cubic metres, may be treated with 900 kg. of common salt, and the solution boiled, when the calcium salt of the 2 : 6-acid separates and is filtered off. On cooling the filtrate to 15°, most of the 2 : 7-salt will have separated, the 1 : 6-salt remaining in solution. The 2 : 7-salt is filtered off and converted into sodium salt as usual (G.P. 48053).

Fierz-David and Hasler (*Helv. Chim. Acta*, 1923, **6**, 1133), studying the proportions of the different disulphonic acids formed at high temperatures, proceeded as follows :

128 gms. of naphthalene was heated to 165°, and while stirring, 200 gms. of 100 per cent. sulphuric acid dropped in during fifteen minutes. Then, at 160°, 400 gms. more " monohydrate " was added, and the solution heated for various periods. The sulphonation having proceeded for the prescribed period, the mixture was then worked up in a manner similar to that described under naphthalene-1 : 5-disulphonic acid. The 2 : 6-acid was precipitated as insoluble barium salt (it had been previously ascertained that the 1 : 5-acid, which also forms an insoluble barium salt, is not present in the sulphonation product under the above conditions), and any mono-sulphonic acid separated and estimated. The results were as follows :

Period of Heating at 160°.	Monosulphonic Acid in Product.	Total Disulphonic Acids.	2:6-Disulphonic Acid.
Hours.	Per Cent.	Per Cent.	Per Cent.
1	13	87	9
2	6	94	10
5	—	100	19
8	—	100	22
11	—	100	24

The filtrate from the 2 : 6-salt was always a mixture of the 2 : 7- and 1 : 6-salts.

1 : 8-**Aminonaphthol**-3 : 6-**disulphonic acid** (H-acid) :
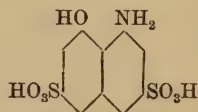
The acid forms colourless crystals, sparingly soluble in cold water. The acid sodium salt (needles, $+1\frac{1}{2}H_2O$) and the acid barium salt (needles, $+4\frac{1}{2}H_2O$) are both sparingly soluble in water. With ferric chloride a brownish-red colouration is obtained. The acid gives a yellow soluble diazo compound.

The preparation of H-acid from naphthalene involves, as shown by the chart on

p. 165, the operations of (1) sulphonation to naphthalene-1 : 3 : 6-trisulphonic acid, (2) nitration of the trisulphonic acid, (3) reduction of the nitro compound, and (4) alkali fusion of the naphthylaminetrisulphonic acid.

Sulphonation.—The main problem lies in the production of the 1 : 3 : 6-trisulphonic acid free from isomers as far as possible. Two of the four disulphonic acids, the 1 : 6- and the 2 : 7-acids, are known to yield the 1 : 3 : 6-trisulphonic acid as sole product on further sulphonation :
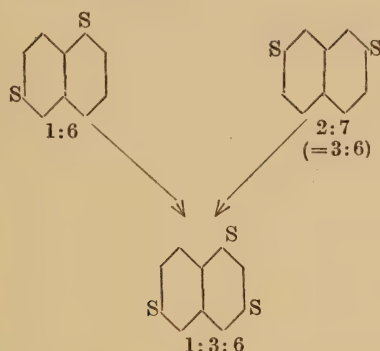
Of the other two disulphonic acids, the 1 : 5-acid yields the 1 : 3 : 5-trisulphonic acid, and the 2 : 6 (=3 : 7)-acid yields the 1 : 3 : 7-trisulphonic acid on further sulphonation. If, therefore, naphthalene could be so sulphonated as to form either the 1 : 6- or the 2 : 7-disulphonic acid, or both, in absence of the 1 : 5- or the 2 : 6-acids, further sulphonation should give the desired 1 : 3 : 6- trisulphonic acid alone.

According to the results obtained by Fierz-David, it is possible to form such a mixture of 1 : 6- and 2 : 7-disulphonic acids. On sulphonating naphthalene with sulphuric acid containing just enough free sulphur trioxide for disulphonation, there is formed at temperatures below 40° a mixture of 1 : 5- and 1 : 6-acids. On heating this mixture to 130° to 135° the 1 : 5-acid gradually disappears, its place being taken by 2 : 7-acid, and if sufficient time is allowed there is obtained within the temperature limits mentioned a mixture of 2 : 7- and 1 : 6-acids. The 2 : 6-acid does not begin to form until about 140°. If these results are correct, then the conditions are indicated for the preparation of the 1 : 3 : 6-trisulphonic acid unmixed with isomers, or containing only a small proportion of them.

In an early patent by Gürke and Rudolph, naphthalene-1 : 3 : 6-trisulphonic acid is prepared, either by adding naphthalene to eight times its weight of 24 per cent. oleum and heating for several hours at 180°, or by adding 1 part of naphthalene to 6 parts of 40 per cent. oleum under 80°, and then heating on the water-bath until the SO_3 has disappeared. By either method considerable quantities of the isomers must be formed.

A process involving three stages is described by Fierz-David ('' Farbenchemie,'' 1920, p. 15), and also in the *Industrial Chemist*, 1925, **1**, 141. Naphthalene is sulphonated first at high temperature to the β-monosulphonic acid, the product is then cooled, and sulphonated further at about the ordinary temperature so as to form the

1 : 6-disulphonic acid as far as possible. By a final period of heating at 160° to 165°, the 1 : 3 : 6-trisulphonic acid is formed to the extent of about 60 per cent.

The most satisfactory method seems to be that given by Fierz-David (" Farben-chemie," second edition, 1923, p. 20).

128 gms. of naphthalene is heated to 165°, and 260 gms. of monohydrate slowly added with good stirring. About ten minutes are required for the addition, after which the temperature is lowered to 125°, at which point it is kept for three and a half to four hours. 420 gms. of 60 per cent. oleum is now added, the temperature being allowed to rise during the addition to 140°. Thereafter the temperature is raised to 170° and kept there for six hours. The solution is then cooled to 15°.

Nitration.—Without isolation, the trisulphonic acid is now nitrated by slowly adding the calculated quantity of nitric acid (103 gms. of 60 per cent. nitric acid), the temperature being maintained at 15° by external cooling. Ten hours' further stirring is given to complete the nitration.

Reduction.—For the reduction of the nitrotrisulphonic acid so formed, either (1) iron may be added to the diluted strongly acid solution, or (2) the diluted solution may be neutralised with chalk or lime and the calcium salt converted into sodium salt, which is then reduced in faintly acid solution with iron. The former method involves less labour than the latter, but gives a lower yield of the amino compound. Both processes will be described.

(1) The nitration mixture is poured into a mixture of 1,500 gms. of ice and 1,500 gms. of water, the temperature of the resulting solution being below 0°. The whole of the iron required for the reduction—180 gms. of iron borings—is added at once, and, with continuous stirring, the reduction proceeds with rise of temperature ulti-mately to about 50°. The iron salt of the 1-naphthylamine-3 : 6 : 8-trisulphonic acid (Koch acid) may separate to some extent. When the reduction is finished (after about eight hours), the solution is warmed to 70°, decanted or filtered from unused iron and sludge, and salt added in quantity sufficient to give a 20 per cent. solution, which salts out the Koch acid. After allowing ten hours for the salting out to be completed, the precipitate is filtered off and washed with 500 c.c. of 15 per cent. salt solution. It is then redissolved in a litre of hot water, neutralised with 50 gms. of chalk, filtered from calcium sulphate and iron oxide, and the Koch acid reprecipitated as acid sodium salt by addition of 150 gms. of salt and 40 gms. of concentrated sulphuric acid. It is then filtered off and pressed. The yield of Koch acid is about 320 gms., as moist press-cake, which, as estimated on a sample by titration with nitrite, corresponds to about 34 gms. of nitrite or an overall yield from the naphthalene of about 50 per cent.

(2) The nitration mixture is poured into 1½ litres of water. The solution heats up to 70° to 80° and nitrous fumes are evolved. 225 gms. (3 mols.) of anhydrous sodium sulphate (or the corresponding quantity of Glauber salt) is added so as to form the sodium salt of the nitrotrisulphonic acid during the subsequent neutralisation. About 650 gms. of limestone or chalk is then added until the solution is neutralised. There is a change of colour from pale to strong yellow at the neutral point. The mixture is filtered and the residue well washed with cold water. The filtrate is made just acid

to Congo paper with dilute sulphuric acid and dropped slowly into a boiling well-stirred mixture of 150 gms. of iron borings (grey cast-iron), $\frac{1}{4}$ litre of water, and 10 c.c. of 40 per cent. acetic acid. The reduction takes about an hour. A drop of the solution on filter-paper should be colourless. Any iron in solution is then precipitated by adding soda ash until the solution is alkaline to litmus (about 5 gms. required). It is then filtered and evaporated to $\frac{3}{4}$ litre. On adding 100 gms. of salt and enough sulphuric acid to make the solution acid to Congo paper, the acid sodium salt of Koch acid is salted out, and is filtered off and pressed. The yield obtained is about 350 gms. of press-cake, corresponding to 35 gms. of nitrite, or 53 per cent. yield on the naphthalene used.

Fusion with Alkali.—In Bayer's original patent (G.P. 69722) it is proposed to convert 1-naphthylamine-3 : 6 : 8-trisulphonic acid into 1 : 8-aminonaphthol-3 : 6-disulphonic acid, either by fusion with twice its weight of caustic soda (containing a little water) in an open vessel at 180° to 190°, or by heating in an autoclave with 30 to 40 per cent. caustic soda solution at 210°.

It has been found that open fusion with alkali is not suitable for substances so easily oxidised as the aminonaphthol-sulphonic acids. The second method of heating with concentrated alkali is, therefore, the one now generally used. In the case of H-acid, however, the temperature of 210° is unnecessarily high, about 180° to 190° being sufficient. Again the strength of the caustic soda solution used is of great importance. Too dilute a solution will readily replace the amino group as well as the 8-sulpho group by hydroxyl. This takes place even with strong caustic soda if the melt is carried on for too long a period. A caustic soda solution of about 35 to 38 per cent. strength gives the most satisfactory results, and the time required will depend on the scale of working.

Continuing the description of the process given by Fierz-David, a stirring autoclave is charged with a quantity of damp press-cake of Koch acid, corresponding to 28 gms. of nitrite (about 280 gms. of press-cake), 130 gms. of caustic soda, and 130 gms. of water, or such a quantity of water as, with the water in the press-cake, will give a caustic soda solution of about 35 per cent. The mixture is then heated with stirring at 178° to 180° for eight hours, the pressure developed being about 7 atmospheres. On opening the autoclave a little ammonia escapes, as it is impossible to avoid replacement of the amino group to a slight extent. The product is dissolved in a litre of water, and 50 per cent. sulphuric acid added till the solution is strongly acid to Congo paper. The H-acid is precipitated as acid sodium salt, and after a few hours is filtered off, washed with 10 per cent. salt solution containing a little acid, pressed, and dried.

The product is analysed in two ways—(1) by titration with standard nitrite solution in acid solution which determines the proportion of NH_2 group present by diazotisation, (2) by titration with standard diazobenzene in alkaline solution which determines the proportion of OH group present by coupling of the diazobenzene in the ortho position to the OH group. The results are conveniently expressed as the weight of product containing 16 gms. of NH_2 and 17 gms. of OH respectively. On a sample of pure H-acid, the two results would, of course, be equal, since each is the molecular

weight in grams of H-acid. On a good specimen of H-acid, the results should agree within 0·5 per cent.

H-acid is used in various capacities in a large number of azo dyes of all classes.

(a) It can be diazotised, and is applied as a first component in several mono- and disazo dyes, in which it is coupled with amines in acid solution. It is not coupled with phenols, because in the alkaline solutions required for such couplings the diazotised H-acid tends to couple with itself (i.e., in the o-position to the hydroxyl group).

(b) It is used as a middle component in polyazo dyes. A diazo compound is coupled in alkaline solution with H-acid. The amino group of the H-acid half of the molecule in the resulting monoazo dye can then be diazotised and coupled with a third component.

(c) H-acid also serves as a middle component in another sense. A diazo compound may be coupled with H-acid in acid solution, when coupling takes place in the o-position to the amino group. A second diazo compound can then be coupled in alkaline solution with the product, in which case the coupling occurs ortho to the hydroxyl group. The typical case of this kind is Naphthol Blue Black :

HO   NH$_2$
—N=N— —N=N— NO$_2$
HO$_3$S   SO$_3$H
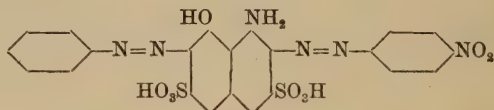
(d) Allied to this use of H-acid is its use in the preparation of certain black and green direct cotton dyes. Thus, Direct Deep Black EW or Chlorazol Black E extra is made by coupling the tetrazo compound of benzidine in acid solution with one molecular proportion of H-acid. Diazotised aniline is then coupled with the product in alkaline solution, coupling taking place in the o-position to the hydroxyl group. Finally, the resulting compound is coupled with one molecular proportion of m-phenylenediamine :

H$_2$N   OH
—N=N— —N=N—
HO$_3$S   SO$_3$H

—N=N— NH$_2$
H$_2$N
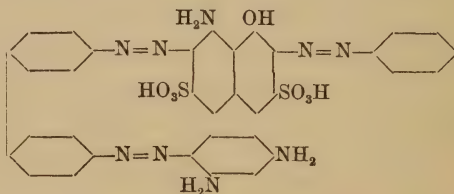
Diamine Green B, on the other hand, is prepared by first coupling diazotised p-nitraniline with H-acid in acid solution, then coupling the tetrazo compound of benzidine with the product (1 molecule) in alkaline solution, and finally coupling with phenol :

HO   NH$_2$
—N=N— —N=N— NO$_2$

—N=N— OH
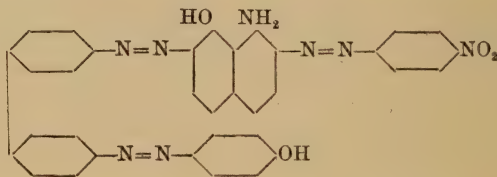
(e) Disazo dyes of bright blue shades are made by coupling the tetrazo compounds of diamines of the benzidine series with two molecular proportions of H-acid in alkaline solution. These are direct cotton colours.

Several other aminonaphthol sulphonic acids resemble H-acid in having the amino and hydroxyl groups in the *peri* position to one another. Most of these are described elsewhere,—*e.g.*, S-acid (p. 156), 2S-acid (p. 158), K-acid (p. 174). These 1 : 8-aminonaphtholsulphonic acids are used, though not so widely as H-acid, for dyes of the same types as those described above, especially for those described in paragraphs (c), (d), and (e). 2S-acid, however, owing to the presence of the sulpho group in the 2-position, is incapable of forming dyes of the (c) and (d) types.

1-**Naphthol**-3 : 6 : 8-**trisulphonic acid** (Oxy-Koch acid) :
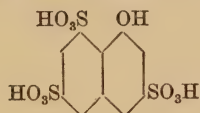
This acid is prepared from 1-naphthylamine-3 : 6 : 8-trisulphonic acid (Koch acid) by diazotisation in a solution strongly acid with sulphuric acid, followed by boiling of the solution of diazo compound until nitrogen is no longer evolved. Naphthasultonedisulphonic acid—
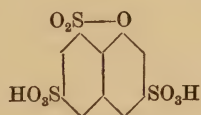
—is thus formed, but on neutralisation of the solution with lime the calcium salt of the naphtholtrisulphonic acid is obtained, and this is then converted into the sodium salt as usual (G.P. 56058).

According to G.P. 71495, Koch acid may be hydrolysed, so as to replace the amino group by hydroxyl, by heating the acid sodium salt with water in an autoclave at 180° to 250°.

The acid is used as an intermediate for azo dyes.

1 : 8-**Dihydroxynaphthalene**-3 : 6-**disulphonic acid** (Chromotrope acid) :
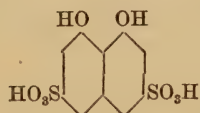
The acid crystallises in needles or leaflets with $2H_2O$, and is easily soluble in water. The disodium salt is easily soluble in water, but can be salted out. The disodium salt is acid to carbonate and a neutral trisodium salt can be formed, as also a tetrasodium salt, which is alkaline in reaction. The alkaline solutions show a violet-blue fluorescence.

Chromotrope acid can be prepared, either from H-acid or from 1-naphthol-3 : 6 : 8-trisulphonic acid, by the action of alkali. According to G.P. 68721 (Bayer), it is made from H-acid by dissolving 15 kg. of the sodium salt in 150 kg. of 5 per cent.

caustic soda solution and heating in an autoclave at 265° for eight hours. The pressure developed is 22·5 atmospheres. After boiling to expel ammonia, the solution is acidified to precipitate the acid sodium salt of chromotrope acid.

The preparation from 1-naphthol-3 : 6 : 8-trisulphonic acid is described in G.P. 67563 (Meister Lucius and Brüning). 13·5 parts of 60 per cent. caustic soda solution is heated at 100° and 17·9 parts of a paste containing 6·65 parts of the sodium salt of the naphtholtrisulphonic acid (or of the sultone, see above) is added, the mixture being then heated at 170° to 220° until foaming ceases. The melt is dissolved in water and acidified to precipitate the acid sodium salt of chromotrope acid.

Chromotrope acid is capable of coupling with 2 molecules of a diazo compound one in each position ortho to a hydroxyl group. It is usually, however, coupled with only 1 molecule of diazotised amine, the resulting dyes, the "chromotropes" of Meister Lucius and Brüning, having the property of dyeing wool from an acid bath, generally in bluish-red shades, which can be afterchromed with bichromate to blue-black or black dyeings of considerable fastness. These dyestuffs also give very level dyeings, a property of importance in dyeing wool.

1 : 8-**Aminonaphthol**-4 : 6-**disulphonic acid** (K-acid) :
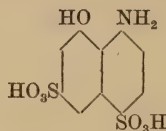
This substance is prepared from naphthalene-1 : 5-disulphonic acid by the same sequence of operations as is used in preparing H-acid from the 1 : 6- and 2 : 7-disul-phonic acids (see Chart, p. 165). In this case, however, it is probably best to start, not from naphthalene, but from the isolated 1 : 5-disulphonate.

In order to form the 1 : 3 : 5-trisulphonic acid from the 1 : 5-disulphonic acid, low temperature sulphonation is required since, although only one trisulphonic acid can be formed, the 1 : 5-disulphonic acid in solution in sulphuric acid undergoes trans-formation to its isomers the 1 : 6- and 2 : 7-acids. The process patented by Kalle and Co. (G.P. 93700, 99164) is as follows : 10 parts of sodium naphthalene-1 : 5-disulphonate is stirred into 40 parts of monohydrate and, at 40°, 9 parts of 70 per cent. oleum dropped in. The mixture is then heated to 80° to 90° until a sample, diluted with water, gives no precipitate on adding salt.

Nitration of the 1 : 3 : 5 (=4 : 6 : 8)-trisulphonic acid to 1-nitronaphthalene-4 : 6 : 8-trisulphonic acid and reduction of this to 1-naphthylamine-4 : 6 : 8-tri-sulphonic acid are carried out, as described under H-acid. Either the acid or the neutral process of reduction may be used. The 1-naphthylamine-4 : 6 : 8-trisulphonic acid is obtained finally as the acid sodium salt, which is readily salted out. In alkaline solution it shows a green fluorescence.

For the conversion of the naphthylaminetrisulphonic acid to aminonaphthol-disulphonic acid, the acid sodium salt obtained from 10 parts of 1 : 5-disulphonate is heated with 20 parts of 75 per cent. caustic soda solution at 140° to 200°, the amino-

naphtholdisulphonic acid being finally precipitated as acid sodium salt by acidifying with hydrochloric acid.

The Bayer process (G.P. 78604, 80741; G.P. Anm. F. 7004, 7006, 7059, K. 11104) differs in several points from that of Kalle and Co. For the sulphonation, 100 parts of sodium naphthalene-1 : 5-disulphonate is stirred into 300 parts of 20 per cent. oleum, the temperature rising to 60° to 80°. The mixture is then heated slowly to 130°. According to the patent, the disulphonate does not dissolve until about this temperature, but then suddenly dissolves, and is converted into trisulphonic acid.

The nitration is carried out as usual, but reduction is performed by the neutral process. For the alkali fusion 75 per cent. caustic soda is used, as in the Kalle process, but the melt is performed in an autoclave at 170° to 175°, this being probably about the best temperature. (The 140° to 200° of the Kalle patent seems to be the ordinary calculated vagueness of such documents.)

As a component of azo dyes, K-acid is used similarly to the other 1 : 8-amino-naphtholsulphonic acids (p. 172).

1-Naphthylamine-3 : 6-**disulphonic acid** (Freund's acid) :
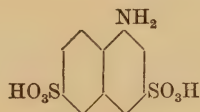
The acid is easily soluble in water and alcohol. The acid sodium salt (needles, $+3H_2O$) and the calcium salt (scales) are soluble in water.

This acid is prepared by nitration of naphthalene-2 : 7-disulphonic acid and reduction of the nitro-acid. The isolated 2 : 7-acid is not usually employed for the purpose, since it is not readily separated from its isomers. Instead, naphthalene is sulphonated so as to produce the maximum proportion of the 2 : 7-acid, which is obtained by sulphonation at 160° to 165°. The mixture of disulphonic acids so formed contains 65 to 70 per cent. of 2 : 7-acid, 20-25 per cent. of 2 : 6-acid, and a little 1 : 6-acid. The preparation is described by Fierz-David ("Farbenchemie," second edition, 1923, p. 26).

128 gms. of naphthalene is heated and stirred at 165°, while 400 gms. of mono-hydrate is added during fifteen minutes. The solution is then heated for an hour at 165° to complete the disulphonation. After cooling to 15°, nitration is carried out as usual with 103 gms. of 60 per cent. nitric acid, the temperature being kept below 30°. The subsequent procedure is similar to that described under H-acid (p. 170), using the "neutral" method of reduction. But 200 gms. of iron powder are used for the reduction, and this is etched with 20 c.c. of concentrated hydrochloric acid instead of acetic acid. The solution of sodium salts of the nitro-acids is acidified with 10 c.c. of hydrochloric acid before adding to the iron for reduction.

When reduction is complete and any dissolved iron precipitated by sodium carbonate and filtered off, the filtrate is evaporated to 800 c.c. and, while boiling, 100 gms. of potassium chloride added, followed by 100 c.c. of hydrochloric acid. On cooling, the acid potassium salt of Freund's acid separates. After twelve hours, this

is filtered off, washed with 200 c.c. of saturated salt solution, and well pressed. The yield is about 270 gms. of dry salt, corresponding to 35 gms. of nitrite, or slightly over 50 per cent. The product may be purified by dissolving in four times its weight of boiling water and allowing to crystallise. The acid sodium salt, which is also sparingly soluble in cold water, is not so suitable for the separation, as it precipitates in a form which is difficult to filter.

The preparation of Freund's acid by a similar method is also given in G.P. 27346 (Freund).

Another method of preparation depends on the fact that the 8-sulphonic acid group in 1-naphthylamine-3 : 6 : 8-trisulphonic acid (Koch acid, p. 170) is easily eliminated by reduction (G.P. 233934, Kalle and Co.) :

9·5 kg. of the acid sodium salt of Koch acid, containing 90 per cent. of diazotisable acid, is boiled with 7·5 kg. of caustic soda solution, 3 kg. of zinc dust, and 90 litres of water for seven hours under reflux. On neutralising with hydrochloric acid and filtering from zinc oxide, acidification of the filtrate precipitates the acid sodium salt of 1-naphthylamine-3 : 6-disulphonic acid.

Freund's acid is used as first component in a few disazo dyes in conjunction with α-naphthylamine or Cleve's acids as middle components.

1-Naphthol-3 : 6-**disulphonic acid :**
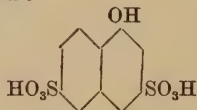
The acid is easily soluble in water. Its alkaline solutions show a pale green fluorescence. The acid sodium salt is readily soluble in water, but can be salted out.

Freund's acid can be converted into the naphthol-disulphonic acid, either by running a solution of the diazo compound into boiling dilute sulphuric acid (G.P. 27346, Freund), or by heating the acid with three times its weight of water at 180° (G.P. Anm. C. 4375, Cassella). Both methods are similar to those by which NW-acid is obtained from naphthionic acid (p. 147).

α-Naphthol-3 : 6-disulphonic acid is also prepared by alkali fusion of naphthalene-1 : 3 : 6-trisulphonic acid.

It is used as end component in a number of azo dyes, chiefly of the monoazo class.

2-Naphthol-7-**sulphonic acid** (F-acid)—

—crystallises in needles from water containing hydrochloric acid, and melts at 89°. It is easily soluble in water and alcohol. Solutions of the salts show a blue fluores-

cence. The sodium salt (needles, $+2\frac{1}{2}H_2O$) is soluble in 12 parts of water at 15°, and can be salted out.

F-acid is prepared by alkali fusion of naphthalene-2 : 7-disulphonic acid. According to G.P. 42112 (Cassella), 100 kg. of sodium naphthalene-2 : 7-disulphonate and 400 kg. of 50 per cent. caustic soda solution are heated together in an autoclave at 225°, until an acidified sample extracted with ether shows traces of the dihydroxy compound in the ether. About ten hours' heating is sufficient. The melt is then dissolved in 1,000 litres of water, acidified with hydrochloric acid, boiled to expel sulphur dioxide, and the solution cooled, when the sodium salt of F-acid crystallises out.

It is possible also to use the mixed sodium salts of naphthalene-2 : 6- and 2 : 7-disulphonic acids, as obtained from the high temperature disulphonation of naphthalene (p. 167). Thus, according to G.P. 45221 (Cassella), 130 kg. of the mixed salts are heated with 35 kg. of caustic soda, 180 litres of water and 40 kg. of common salt in an autoclave at 240° to 270° for sixteen hours. A mixture of the salts of 2-naphthol-6-sulphonic acid (Schäffer acid) and F-acid is thus formed, and the mixed sodium salts may be isolated as above. After amidation, as described under 2-naphthylamine-7-sulphonic acid, the mixture is used for azo dyes.

The two acids, however, can be separated. The alkaline melt from the autoclave contains the two disodium salts of the acids $[C_{10}H_6(ONa).SO_3Na]$, and that of Schäffer acid mostly separates from the melt along with the sodium sulphite. It is filtered off, and the monosodium salt of F-acid obtained from the filtrate by acidifying. Or the whole melt may be dissolved in 500 litres of water, acidified with hydrochloric acid and boiled to expel sulphur dioxide. The boiling solution is then saturated with salt, which throws out the Schäffer salt, and after filtering hot, the filtrate, on cooling, gives crystals of the F-salt.

While formerly used for azo dyes, this use seems now to be restricted to its addition in small proportion to β-naphthol in order to obtain a modified shade of Para Red. F-acid is mostly converted into the corresponding naphthylaminesulphonic acid (also called F-acid, or the two are sometimes distinguished by the names Oxy-F- and Amido-F-acid).

2-**Naphthylamine**-7-**sulphonic acid** (Amido-F-acid):

The acid crystallises in needles or prisms with $1H_2O$ from lukewarm water, but this monohydrate loses water at 100° (on boiling with water), forming the anhydrous acid as a sparingly soluble sandy powder, soluble in 350 parts of boiling water. The sodium salt crystallises with $4H_2O$ and dissolves in 70 parts of cold water, but is easily soluble in hot water and in 96 per cent. alcohol. The barium salt is sparingly soluble. Solutions of the salts show a red-violet fluorescence.

This acid is best prepared by Bucherer's method—that is, by heating the sodium salt of F-acid with ammonium sulphite and ammonia in an autoclave at about 150° (Bucherer, *J. pr. Chem.*, **70**, 357).

The amidation of F-acid with ammonia alone at 250° is described in G.P. 43740 (Cassella).

Amido-F-acid is used as an end component in azo dyes, usually in conjunction with tolidine as first component.

1 : 5-**Dihydroxynaphthalene**—
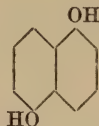
—crystallises in colourless leaflets from water, and sublimes in long needles, m.p. 258° to 260°. It is sparingly soluble in water, easily soluble in alcohol, but almost insoluble in benzene. It is stable in air, but in alkaline solution oxidises quickly.

Its preparation from naphthalene-1 : 5-disulphonic acid is described by Ewer and Pick (G.P. 41934).

100 kg. of sodium naphthalene-1 : 5-disulphonate is stirred with 300 to 400 kg. of caustic soda at 220° to 260° in an open cast-iron pan, or in an autoclave at the same temperature, enough water being added to give a thick paste. (Presumably the latter method is preferable in view of the sensitivity of alkaline solutions of the dihydroxy compound to air.) 1-Naphthol-5-sulphonic acid, as sodium salt, is formed as an intermediate stage in the reaction. Tests are carried out on the melt as follows : 5 gms. of the melt is dissolved in 200 gms. of water, and the solution filtered and cooled. To 100 c.c. of the solution sodium bicarbonate is added till a slight cloudiness appears : about 7 gms. of bicarbonate being required. A solution of diazotised benzidine is then added until a drop on filter-paper spotted on the colourless rim with sodium naphthionate solution shows a pale brown colouration. The remaining 100 c.c. of solution is then added, followed by 10 gms. of bicarbonate. If the melt is completed, the whole of the azo dye formed in the test separates in blue flocks. The solution should not be violet.

The melt is now run into the calculated quantity of dilute hydrochloric or sulphuric acid. On cooling, the dihydroxynaphthalene separates in nearly white dense flocks.

Another method of preparation, from Laurent's acid, is given on p. 159.

This intermediate gives, by coupling with diazotised o-aminophenol-p-sulphonic acid, an azo dye which can be afterchromed on wool to a black of exceptionally good shade and fastness, named Diamond Black PV.

Naphthylaminedisulphonic Acids derived from Naphthalene-1 : 5 and 1 : 6-Disulphonic Acids.

When the mixture of 1 : 5- and 1 : 6-disulphonic acids, obtained by the sulphonation of naphthalene, as described on pp. 166 and 167, is nitrated, each disulphonic acid yields both an α- and a β-nitrodisulphonic acid as follows :
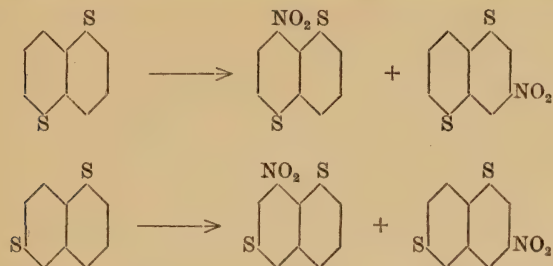
On reduction, the nitro-acids give a mixture of the corresponding naphthylaminedisulphonic acids from which the 1 : 3 : 8- and 1 : 4 : 8-naphthylaminedisulphonic acids may each be separated. As to the separation of the 2 : 4 : 8- and 2 : 4 : 7-naphthylaminedisulphonic acids, little information has been published, though the former is known to be used as first component in azo dyes. The proportions of the 1 : 3 : 8- and 1 : 4 : 8-acids obtainable may be varied by alteration of the temperature of sulphonation of the naphthalene so as to vary the proportions of 1 : 5- and 1 : 6-disulphonic acids in the mixture, and details of the method of separation must be altered to suit the varying proportions.

A method of separation of the two α-naphthylaminedisulphonic acids is described by Paul (*Zeit. angew. Chem.*, 1896, **9,** 559). The preliminary sulphonation is carried out by adding 280 kg. of oleum slowly during four to five hours to 100 kg. of molten naphthalene at 80°. The finished sulphonation mixture is then cooled to 30° and 100 kg. of 60 per cent. nitric acid (*i.e.,* 20 per cent. excess) is added during eighteen hours, while the temperature is maintained at 20° to 30°. The nitration mixture is now run into milk of lime made from 170 kg. of lime and 1,000 kg. of water. The mixture is boiled and filtered from gypsum. The calcium salts of the nitro-acids are converted into sodium salts, and the solution of these evaporated to a volume of 1,500 litres.

The reduction is effected in an unusual way. The solution of sodium salts is boiled and, while stirring, 200 kg. of iron borings added. 100 kg. of sulphuric acid (66° Bé) is then run in slowly over two and a half hours, and boiling continued for a further two to three hours, with addition of more iron if necessary to complete the reduction. After neutralising the solution with slaked lime and converting the solution of calcium salts into sodium salts, the liquid is evaporated till it reaches 28° Bé, and then allowed to stand for eight days. The sodium salt of 1-naphthylamine-4 : 8-disulphonic acid crystallises out. It may be purified by dissolving in about four times its weight of hot water, cooling to 40°, filtering from any sparingly soluble sodium salt of Peri acid (from any α-sulphonic acid in the original sulphonation mixture), and acidifying with hydrochloric acid, when the acid sodium salt precipitates.

The filtrate from the 1 : 4 : 8-acid is diluted with 1,000 litres of water, and 600 kg. of salt and 480 kg. of hydrochloric acid added. It then shows 28° Bé. After standing for some time, the acid sodium salt of 1-naphthylamine-3 : 8-disulphonic acid separates. It is recrystallised with the aid of salt.

The yield of each acid is about 20 per cent.

The final filtrate contains 2-naphthylamine-4 : 7- and 4 : 8-disulphonic acids.

Another method of separation of the 1 : 4 : 8- and 1 : 3 : 8-acids is given in E.P. 161859 (South Metropolitan Gas Co.). It depends on the difference in solubility of the barium salts of the acids. A suitably concentrated solution of the neutral sodium salts of the mixed acids is boiled with enough barium chloride to convert all the acids present to barium salts. The barium salt of the 1 : 4 : 8-acid is precipitated, and is filtered off from the hot liquid and washed. The filtrate and washings are acidified with hydrochloric acid, which precipitates the acid barium salts of the 1 : 3 : 8-acid. This is filtered off from the still hot liquor in order to keep in solution the salts of the 2 : 4 : 7- and 2 : 4 : 8-acids.

1-Naphthylamine-4 : 8-disulphonic acid has already been described (p. 156) in connection with another method of preparation.

1-**Naphthylamine**-3 : 8-**disulphonic acid**—
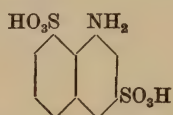
—crystallises in scales with 1H$_2$O, very soluble in hot water. Its acid sodium salt (needles, +6H$_2$O) is soluble in 30 parts of cold water. Its disodium salt (needles, +6H$_2$O) is very soluble in water. It gives a colourless sparingly soluble diazo compound.

This acid is not used as an azo component, but is converted into the corresponding naphtholdisulphonic acid.

1-**Naphthol**-3 : 8-**disulphonic acid** (ε-acid):
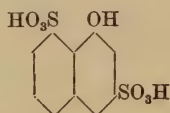
The disodium salt (prisms, +6H$_2$O) is soluble in 5·5 parts of cold water.

1-Naphthylamine-3 : 8-disulphonic acid may be converted into ε-acid in two ways :

(a) 36 kg. of the acid sodium salt of the naphthylaminedisulphonic acid is dissolved in 500 litres of cold water with the aid of 4 to 5 kg. of caustic soda. The solution is acidified with 20 kg. of concentrated sulphuric acid, and then diazotised with 7 kg. of sodium nitrite dissolved in 75 litres of water. The sparingly soluble diazo compound mostly separates. The mixture is now boiled until evolution of nitrogen ceases. On cooling, the sodium salt of the sultonesulphonic acid crystallises in long colourless needles (+3H$_2$O) :
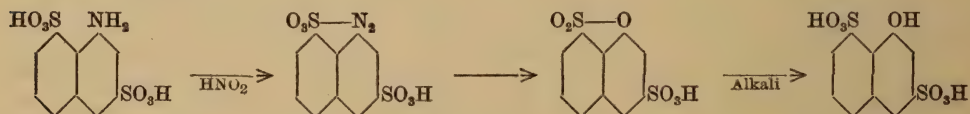
The sultone is easily converted into the sodium salt of the naphtholdisulphonic acid by warming with the necessary quantity of caustic soda solution (G.P. 52724, Ewer and Pick).

A variation of this method (G.P. 45776, A.G.F.A.) is to filter off the diazo compound, then to stir with water containing a little sulphuric acid, and boil as before. Instead of isolating the sultone, the hot solution is neutralised with lime (this also hydrolyses the sultone), filtered from calcium sulphate, converted into sodium salt in the usual way, and evaporating the solution to crystallising point, when, on cooling, long colourless prisms of the disodium salt of ε-acid separate.

(*b*) The amino group may also be replaced by hydroxyl by a method analogous to that by which α-naphthylamine is converted into α-naphthol.

The acid sodium salt of 1-naphthylamine-3 : 8-disulphonic acid is heated with four times its weight of water in an autoclave at 180° for five to eight hours. The ε-acid is isolated by salting out or by evaporation (G.P. 71494, Meister Lucius and Brüning).

ε-Acid is used as an end component in mono-, dis-, and trisazo dyes.

CHAPTER XII

DERIVATIVES OF β-NAPHTHOL

In contrast with α-naphthol, β-naphthol is not only itself an important dyestuff intermediate, but gives rise to a considerable number of useful intermediates, which are mostly derived by sulphonation. These intermediates are almost entirely used as end components in azo dyes. The reason for the extensive use of β-naphthol and its sulphonic acids as compared with α-naphthol lies in the fact that coupling with β-naphthol takes place in the α-position, giving azo compounds of the general formula I, whereas with α-naphthol it takes place in the 4-position (formula II) :

It is found that the *p*-hydroxyazo compounds (II) are useless as dyestuffs because of their lack of fastness and intensity, and also their sensitivity to alkalies. The *o*-hydroxyazo dyes, on the other hand, show great intensity and brightness of shade, little or no sensitivity to alkalies, and a fair degree of fastness. Only those α-naphtholsulphonic acids in which the presence of a sulphonic acid group in the 4-position (or the 3- or 5-positions), as in NW-acid, Freund's acid, etc., forces the coupling to take place in the 2-position, yield azo dyes of practical value.

Sulphonation of β-Naphthol.

β-Naphthol is very easily attacked by sulphuric acid even in the cold. At temperatures below 15° there seems to be first formed a sulphuric ester (I) which, however, if actually formed, rapidly transforms to the 1-sulphonic acid (II), and this in turn to the 8-sulphonic acid (III) :

At slightly higher temperatures the 8-sulphonic acid (Crocein acid) transforms to the 6-sulphonic acid (Schäffer acid), which is the most stable of the monosulphonic acids obtained by direct sulphonation of β-naphthol, and persists without further transformation until disulphonation occurs. The transformation of the 8- to the 6-sulphonic acid is not quite complete at any temperature, but mixtures of the two acids in equilibrium at definite temperatures are obtained. The proportion of the 8-sulphonic acid diminishes as the temperature rises.

Using sufficient sulphuric acid for disulphonation, two disulphonic acids are

CHART X.—DERIVATIVES OF β-NAPHTHOL.

formed—namely, β-naphthol-6 : 8-disulphonic acid (G-acid) and β-naphthol-3 : 6-disulphonic acid (R-acid):
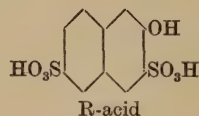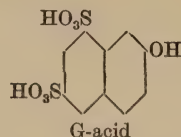
G-acid preponderates at temperatures below 50°, but diminishes in proportion as the temperature of sulphonation rises. Further sulphonation produces β-naphthol-3 : 6 : 8-trisulphonic acid.

2-Naphthol-1-sulphonic acid :
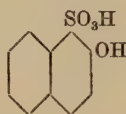
The sodium salt crystallises from diluted alcohol in leaflets which are easily soluble in water.   The acid is unstable and readily hydrolyses back to β-naphthol.

This acid is formed as described in G.P. 74688 (Tobias) by adding 1 part of β-naphthol to 2 to $2\frac{1}{2}$ parts of sulphuric acid (90 to 92 per cent.).   The temperature is allowed to rise to 40°, and kept there for ten minutes.   The mass solidifies.   After diluting with water, the sodium salt may be obtained by salting out, or through the calcium salt in the usual way.

But, as obtained in this way, it is contaminated with the 8- and 6-sulphonic acids. Probably the best method of obtaining the 1-sulphonic acid free from isomers is to use Armstrong's method of sulphonation with chlorsulphonic acid. β-Naphthol is dissolved in carbon disulphide and the calculated quantity of chlorsulphonic acid added.   When sulphonation is finished, the solvent is evaporated off.

It has been proposed to use this acid in place of β-naphthol for developed colours (Calico Printers' Association and Fourneaux, G.P. 204702).   It would give colours identical with those obtained from β-naphthol, since coupling with diazo compounds takes place in the 1-position, the sulpho group being eliminated.   It would have the advantage of solubility in water.

It is mainly used, however, for the production of the corresponding naphthylamine-sulphonic acid.

2-Naphthylamine-1-sulphonic acid (Tobias acid):
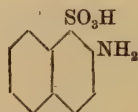
The acid crystallises in needles, sparingly soluble in cold water, but more soluble in hot water.   The sodium salt is easily soluble in water, but can be salted out.   The diazo compound is yellow and sparingly soluble in water.

Amidation of the naphtholsulphonic acid by ammonia alone or by **ammonium**

chloride and ammonia at temperatures over 200° does not give good results. Some β-naphthylamine is formed owing to the instability of the acid.

This can be avoided by using the Bucherer reaction (*J. pr. Chem.*, 1904 [2], **70,** 357). The sodium salt of the naphtholsulphonic acid is heated with 40 per cent. ammonium sulphite and 20 per cent. ammonia at about 150°, the Tobias acid being isolated by acidifying the product.

Tobias acid is particularly well suited for the preparation of lake pigments—for example, Lithol Red, which is obtained by coupling diazotised Tobias acid with β-naphthol.

2-**Naphthol**-8-**sulphonic acid** (Crocein acid):
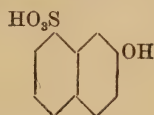
The acid is soluble in water. On boiling the aqueous solution, the acid is hydrolysed to β-naphthol and sulphuric acid. The monosodium salt crystallises in leaflets, easily soluble in water, sparingly in alcohol. The disodium salt forms needles containing $2C_2H_6O$ when crystallised from alcohol.

2-**Naphthol**-6-**sulphonic acid** (Schäffer acid):
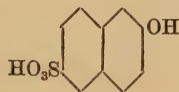
The acid crystallises in leaflets, m.p. 125°, soluble in water and alcohol. The sodium salt (leaflets, $+2H_2O$) dissolves in 58 parts of water at 14° and in 3·3 parts at 80°. It is insoluble in alcohol. The calcium salt (leaflets, $+5H_2O$) dissolves in 30 parts of water at 18°, and is soluble in alcohol.

These two acids are conveniently described together since, as already mentioned, they are in general formed together, although, according to G.P. 33857, by sulphonating 1 part of β-naphthol with 2 parts of sulphuric acid at 20°, which requires about seven days, very little Schäffer acid is formed.

The sulphonation is usually carried out at 50° to 60°, as described in G.P. 18027, 20397 (Bayer). Dry and finely powdered β-naphthol is stirred quickly into twice its weight of concentrated sulphuric acid. Heat is developed, but the temperature is not allowed to rise above 60°. Stirring at 50° to 60° is continued until sulphonation is finished. The solution is then poured into twice its weight of water.

The salts of the two acids may now be separated to some extent, either by neutralising the solution with soda ash, or by adding two-thirds of the calculated quantity of caustic soda. In either case about four-fifths of the Schäffer salt separates, the Crocein salt remaining in solution with the rest of the Schäffer salt. A better separation can be obtained by neutralising the solution with lime, converting the calcium salts into sodium salts and evaporating the solution of sodium salts to dryness. On extracting the dry salts with 3 to 4 parts of 90 per cent. alcohol at the boil, the Crocein salt dissolves, and is filtered hot from the undissolved Schäffer salt.

The Schäffer salt in these ways can be obtained fairly pure—at any rate, after a recrystallisation or salting out from water. But the Crocein salt is always obtained mixed with some Schäffer salt. However, by taking advantage of the difference in the rates of coupling of the two salts with diazo compounds, it is possible to remove the remaining Schäffer salt. Crocein salt, probably owing to the presence of the sulpho group in the 8-position, couples with diazo compounds much more slowly than Schäffer salt, and in a mixture of the two it is possible to obtain coupling with the whole of the Schäffer salt before any reaction takes place with the Crocein salt. Moreover, the azo dyes formed with the Schäffer salt are more readily salted out.

An aliquot part of the solution of Crocein salt and Schäffer salt, left after removal of the main quantity of Schäffer salt, is diluted with water, acidified with a few drops of acetic acid, and titrated with $\frac{N}{10}$ p-nitrobenzenediazonium chloride solution (containing sufficient sodium acetate to render it neutral to Congo paper). With practice, the point at which coupling of the diazo compound with the Schäffer salt is complete may readily be found, the red monoazo dye formed being salted out by the addition of half-saturated salt solution. The main quantity of the solution of Crocein and Schäffer salts is then treated with the calculated quantity of a diazo compound to couple with the Schäffer salt, the dye salted out, and the remaining solution of Crocein salt used direct for making azo dyes.

Preparation of Schäffer Acid in Conjunction with R-Acid.

It is possible to sulphonate β-naphthol so as to produce a mixture of Schäffer acid and R-acid. The method is described by Fierz-David (" Farbenchemie," 1920, p. 42). Into 200 gms. of 100 per cent. sulphuric acid 142 gms. of pure finely powdered β-naphthol is stirred. The temperature rises rapidly to about 80°, and stirring is continued for a quarter of an hour till the mass becomes homogeneous. The temperature is then raised to 100° to 110°, and is kept at this point until a test portion no longer shows separation of β-naphthol on pouring into water. This requires about three hours' heating. The solution is then poured into 1 litre of water and neutralised with about 200 gms. of chalk. Without filtering, the calcium salts are converted into sodium salts by adding a warm solution of sodium sulphate until a filtered sample gives no precipitate with sodium sulphate. The mixture is then filtered and the residual calcium sulphate well washed. The solution of sodium salts is evaporated to $\frac{1}{2}$ litre, and sufficient salt added to form a 20 per cent. solution. The solution is then cooled and stirred for a day, when the Schäffer salt separates completely. It is filtered off and washed with a little salt solution. It contains a very small proportion of R-salt, as shown by a slight fluorescence of its aqueous solution. The yield is 160 gms. of 100 per cent. Schäffer salt.

On acidifying the filtrate with concentrated sulphuric acid and allowing to stand for a long time, the acid sodium salt of R-acid separates. About 80 gms. of R-salt are obtained.

Schäffer acid is used as an end component chiefly in monoazo dyes for wool of

red and bordeaux shades. A nitroso derivative is also made whose iron salt is used for fast green shades on wool.

Crocein acid is used like Schäffer acid, but gives yellower shades of red.

2-**Naphthylamine**-6-**sulphonic acid** (Brönner acid):

The acid crystallises in leaflets ($+1H_2O$), soluble in 2,500 parts of cold or 260 parts of boiling water. Solutions of the acid or its salts show a blue fluorescence. The salts are mostly sparingly soluble. The sodium salt (leaflets, $+2H_2O$) dissolves in about 40 parts of cold water. The calcium and barium salts are much less soluble.

Brönner acid is prepared by the amidation of Schäffer acid, using Bucherer's method. Schäffer salt (50 parts) is heated with 75 per cent. ammonium sulphite solution (8 parts) and 20 per cent. ammonia (74 parts) at 200° for six hours. On acidifying the product, Brönner acid is precipitated.

Brönner acid is used chiefly as a *first* component in azo dyes, giving, for example, a scarlet by coupling its diazo compound with β-naphthol.

2-**Naphthol**-3 : 6-**disulphonic acid** (R-acid):

The acid forms silky deliquescent needles, very soluble in water and alcohol. The **sodium salt** crystallises in aggregates of minute needles, soluble in cold water, but sparingly soluble in alcohol and in brine. The **barium salt** crystallises in needles ($+6H_2O$), soluble in 12 parts of boiling water, but insoluble in alcohol. Solutions of the salts show a bluish-green fluorescence.

2-**Naphthol**-6 : 8-**disulphonic acid** (G-acid):
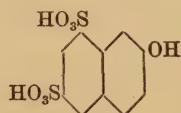
Very little information has been published regarding this acid or its salts. The **potassium salt** is said to be soluble in 2·5 parts of boiling water. The **sodium salt** is soluble in 80 per cent. alcohol. Apart from the potassium salt, the salts of G-acid are much more soluble in water than those of R-acid.

These two acids are formed together when β-naphthol is sulphonated with sufficient sulphuric acid (3 to 4 parts, according to the strength of the acid) to form disulphonic acid. G-acid preponderates at low temperatures, while R-acid is the main product at temperatures of 100° and upwards.

In the original patent describing their preparation (G.P. 3229, Meister Lucius and Brüning), 10 kg. of β-naphthol and 30 kg. of concentrated sulphuric acid are

heated together for twelve hours at 100° to 110°.   The sulphonic acids are converted to their sodium salts, which are dried and digested with 3 to 4 parts of 75 to 85 per cent. alcohol.   G-salt dissolves, while R-salt remains undissolved.

Apart from the expense of this method of separation, it was found to be unsatisfactory, since R-salt dissolves to some extent and the G-salt obtained is, therefore, impure.   A later patent, G.P. 33916 (Beyer and Kegel) describes a simpler process which was adopted generally on the manufacturing scale.   The sulphonation mixture, prepared by heating β-naphthol with four times its weight of concentrated sulphuric acid at 125° to 150° for five to six hours, was poured into hot water, the solution neutralised with soda and saturated with common salt.   On cooling, most of the R-salt separated.

This method yields a fairly pure R-salt, but the G-salt remaining in the filtrate is accompanied by substantial quantities of R-salt and possibly also Schäffer salt.   These latter compounds, however, can be removed by the method used for removing Schäffer salt from Crocein salt (p. 186), since G-salt, owing to the presence of the sulpho group in the 8-position, like Crocein salt, only couples very slowly with diazo compounds, whereas R-salt couples readily and quickly, and the azo dyes formed are easily salted out.

The relative importance of R- and G-acids has changed since the above patents were published, G-acid having become increasingly important as a source of the much-used Gamma-acid (see Chart X., p. 183).   Sulphonation is, therefore, carried out at as low a temperature as possible in order to obtain the maximum proportion of G-acid. Such a process is described by Fierz-David ("Farbenchemie," 1920, p. 44), the separation of the two acids depending on the sparing solubility of the acid potassium salt of G-acid.

142 gms. of finely powdered β-naphthol is added slowly to 420 gms. of 100 per cent. sulphuric acid, which is well stirred.   The temperature is kept between 30° and 35°. Stirring is continued until a sample on dilution with a little water no longer gives a precipitate.   If this point is not reached in two days, a little more monohydrate is added, or, very cautiously, some 15 per cent. oleum.   The solution is now poured into 1 litre of water and neutralised with chalk or milk of lime, the calcium sulphate being then filtered off.   The potassium salts are then formed by adding to the filtrate, either potassium carbonate (about 150 gms.) or the cheaper commercial 90 per cent. potassium sulphate, until the calcium is completely precipitated as carbonate or sulphate, which is filtered off.   The solution of potassium salts is evaporated to 400 c.c., and sufficient hydrochloric acid (about 100 gms.) added to make it strongly mineral acid.   On cooling, the acid potassium salt of G-acid separates in fairly pure condition and, after standing for a day, is filtered off, washed with a little 10 per cent. potassium chloride solution, and well pressed.   The mother liquor, containing the R-salt, is either salted out with 150 gms. of salt or is used directly for azo dyes.

The yields obtained are 160 gms. of G-salt (as acid potassium salt, M.W. 341), and 145 gms. of R-salt (M.W. 341).

A different method of separation is proposed in E.P. 210120 (C. L. Masters, Southern Dyestuffs Co., U.S.A.), and is claimed to give very pure G- and R-salts.

It depends on the facts that the dipotassium salt of G-acid is very sparingly soluble in a concentrated solution of the dipotassium salt of R-acid, and that on boiling the dipotassium salt of R-acid with excess of calcium hydroxide, an almost insoluble basic calcium potassium salt is precipitated.

β-Naphthol (1,152 lbs.) is sulphonated with $3\frac{1}{2}$ to 4 parts of sulphuric acid (66° Bé) for forty-eight to sixty hours at about 60°. The finished sulphonation melt is run into sufficient water to make a 20 per cent. sulphuric acid solution, 1,392 lbs. of potassium sulphate added, and the solution boiled for a short time. Sufficient milk of lime (made from about 2,300 lbs. of quicklime) is then added to neutralise the acid, and the calcium sulphate filtered off. The filtrate, which contains the potassium salts of the sulphonic acids, is concentrated to the point of incipient crystallisation, filtered to remove a little calcium sulphate and allowed to cool. The G-salt, which crystallises out, is filtered off, washed free of R-salt by means of a little saturated potassium sulphate solution, and dried.

The filtrate is boiled up for a short time with milk of lime, made from about 170 lbs. of quicklime. The basic calcium potassium salt of R-acid which precipitates is filtered off, washed free of soluble impurities, and suspended in 3,500 lbs. of water. Sulphuric acid is added to precipitate the calcium as sulphate, which is filtered off. The R-salt is then salted out from the filtrate by adding 525 lbs. of common salt.

R-acid is used as an end component in a large number of mono-, dis-, and trisazo dyes. The mono- and disazo dyes are generally red in shade.

G-acid is also used as an end component in the same classes of azo dyes as those for which R-acid is used, though to a much smaller extent. The shades produced are yellower than those produced from R-acid, a difference expressed in the naming of the acids (G=*gelb*, R=*rot*). G-acid is further applied in the preparation of a diphenyl-naphthylmethane colour (Wool Green S) by condensing it with Michler's hydrol.

2-**Naphthylamine**-3 : 6-**disulphonic acid** (Amido-R-acid)—

—and 2-**Naphthylamine**-6 : 8-**disulphonic acid** (Amido-G-acid)—
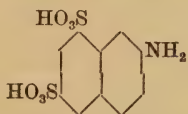
—can be prepared by heating R-acid and G-acid respectively with **ammonia** and **ammonium sulphite** (Bucherer reaction).

Amido-R-acid is applied both as a first and as an end component in azo dyes, but chiefly in the latter capacity, since diazo compounds couple readily with it in the 1-position.

Amido-G-acid, on the other hand, is useless as an end component, owing to the presence of the sulpho group in the 8-position, which practically inhibits coupling with

diazo compounds. It is, however, used as a first component in polyazo dyes. Its largest application is to the preparation of Gamma-acid, which is described on p. 194.

β-**Naphthylamine**—

—crystallises from water in lustrous leaflets, m.p. 112°, b.p. 294°. It has no smell. It is sparingly soluble in cold, but easily in hot water, and in alcohol and ether. It is moderately volatile in steam.

Its **hydrochloride**, $C_{10}H_7.NH_2.HCl$, forms leaflets, easily soluble in water and alcohol. Its **sulphate**, $(C_{10}H_7NH_2)_2.H_2SO_4$, is sparingly soluble in water. Its acetyl compound melts at 134° to 136°.

β-Naphthylamine is prepared by Bucherer's method (*J. pr. Chem.* [2], **69,** 88; G.P. 117471) from β-naphthol by heating 100 parts of the naphthol with 150 parts of 40 per cent. ammonium sulphite solution and 100 parts of 20 per cent. ammonia in an autoclave with stirrer at 150° for eight hours. The pressure developed is about 6 atmospheres. On cooling, the β-naphthylamine separates as a solid cake, which is broken up, filtered, and washed with water. The crude product contains some unchanged β-naphthol and some ββ′-dinaphthylamine :
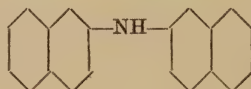
It is purified by dissolving in water and the necessary hydrochloric acid (free from sulphuric acid), filtering from undissolved β-naphthol, and precipitating as sulphate by adding a concentrated solution of sodium sulphate. After standing for some time to complete the precipitation, the sulphate is filtered off, washed with cold water, and dried. The base may be isolated by stirring the sulphate with water, and a slight excess of sodium carbonate, but the sulphate is generally used directly for the preparation of β-naphthylaminesulphonic acids, etc. A further purification, especially from dinaphthylamine (b.p. 471°), can be carried out by vacuum distillation of the base. The yield is about 85 per cent.

With a view to lessening the cost of production of β-naphthylamine, it has been proposed by Campbell (*J. Soc. Dy. Col.*, 1922, **38,** 114), and by Galbraith, etc. (E.P. 184284), to use instead of pure β-naphthol the crude melt obtained by the fusion of naphthalene-β-sulphonic acid with caustic soda (p. 160). This, of course, contains sodium sulphite formed in the fusion, and it is only necessary to add an ammonium salt in order to obtain the mixture of β-naphthol, ammonium sulphite, and ammonia required for the amidation. The process, as described in the above patent, is carried out as follows : An autoclave is charged with 4,800 gms. of the crude naphthol melt, 2,953 gms. of ammonium chloride, 2,617 c.c. of aqueous ammonia (D 0·880), and 9,280 c.c. of water. It is then heated at 170° for fourteen hours, the maximum pressure being 180 lbs. After cooling, the excess of ammonia is blown off and the β-naphthylamine isolated, as already described. Any unchanged β-naphthol

is removed by two extractions with caustic soda solution.   The base is then distilled under reduced pressure, and a 79·7 per cent. yield of β-naphthylamine obtained.

β-Naphthylamine is used as an end component in a few azo dyes.   It is also used in **naphthylating** Rosaniline, thus producing blue dyes analogous to the Aniline Blues. A vat dye, Indanthrene Red BN, is made by condensing β-naphthylamine with 1-chloroanthraquinone-2-carboxylic acid, the condensation taking place between the amino group of the β-naphthylamine and the chlorine atom.   The formation of the dyestuff is further explained on p. 212.   The main use for β-naphthylamine consists in its sulphonation to the 6 : 8- and 5 : 7-disulphonic acids from which Gamma- and J-acids are prepared.   This is dealt with in the following pages.

Sulphonation of B-Naphthylamine.

While β-naphthylaminesulphonic acids can, in several cases, be prepared by amidation of the corresponding β-naphtholsulphonic acids—*e.g.*, Brönner acid (p. 187), amido-F-acid (p. 177), Amido-R-acid (p. 189), Amido-G-acid (p. 189), the sulphonation of β-naphthylamine provides an equally convenient method of preparing some of these acids, and in addition makes possible the preparation of certain sulphonic acids, which cannot be obtained through the sulphonation of β-naphthol.   Thus, while 2-naphthylamine-6 : 8-disulphonic acid (Amido-G-acid) can be prepared by either method, 2-naphthylamine-5 : 7-disulphonic acid can only be obtained by the sulphonation of β-naphthylamine.   It is principally with the object of preparing these two disulphonic acids that the sulphonation of β-naphthylamine is carried out on the manufacturing scale, though 2-naphthylamine-1 : 5-disulphonic acid and the 3 : 6 : 8-trisulphonic acid are also made in this way and used to some extent.   The 6 : 8- and 5 : 7-disulphonic acids are required for the preparation of Gamma-acid (2-amino-8-naphthol-6-sulphonic acid) and J-acid (2-amino-5-naphthol-7-sulphonic acid) respectively, two widely used intermediates for azo dyes.   The sulphonation of β-naphthylamine will, therefore, be considered from the point of view of the preparation of these two disulphonic acids.

β-Naphthylamine is sulphonated by three to four times its weight of 94 to 100 per cent. sulphuric acid to a mixture of monosulphonic acids, whose composition varies with the temperature of sulphonation (Green and Vakil, *J.C.S.*, 1918, **113,** 35).   At temperatures under 100°, a mixture of the 5- and 8-sulphonic acids (about 60 per cent. of the 5- and 40 per cent. of the 8-acid) with traces of the 6- and 7-sulphonic acids is formed.   At temperatures of 150° and upwards about equal proportions of the 6- and 7-sulphonic acids are obtained.   The 8-sulphonic acid slowly transforms to the 5-acid on long heating in sulphuric acid solution.   The monosulphonic acids are almost insoluble in water, but their sodium salts are readily soluble.   The 8-acid may be separated from the others by the insolubility of its sodium salt in 90 to 95 per cent. alcohol, the sodium salts of the others being soluble (G.P. 29084, Dahl and Co.).

Disulphonation is obtained by the use of a large excess of oleum.   The published information on this point is chiefly due to Fierz-David (" Farbenchemie," 1920, pp. 45-51; second edition, 1923, p. 43; *Helv. Chim. Acta*, 1923, **6,** 1146), who has

shown that disulphonation can be carried to completion at about 55°, when a mixture of the 6 : 8- and the 5 : 7-disulphonic acids, together with some 1 : 5-disulphonic acid is formed. These may be separated under certain definite conditions by the difference in solubility of the acids in dilute sulphuric acid, the 6 : 8-disulphonic acid being the least soluble and the 1 : 5-acid the most soluble. An improved method of separation is obtained by using a larger excess of sulphuric anhydride and sulphonating finally at 85°, when the 5 : 7- and 1 : 5-disulphonic acids are converted into the 1 : 5 : 7-trisulphonic acid, while the 6 : 8-disulphonic acid remains unaffected. The 6 : 8-disulphonic acid is then readily separated from the much more soluble trisulphonic acid. The latter, on heating its dilute sulphuric acid solution to the boil, loses the 1-sulphonic acid group by hydrolysis, yielding the 5 : 7-disulphonic acid. The relations between the various sulphonic acids are indicated by the following scheme :

(S = SO₃H)
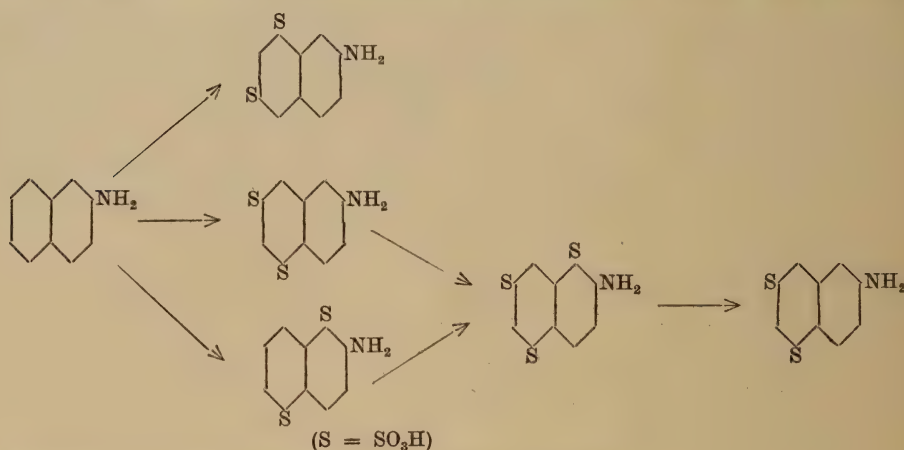
2-**Naphthylamine**-6 : 8-**disulphonic acid** (Amido-G-acid):
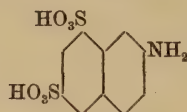
The acid crystallises with $4H_2O$ in small fine needles. Solutions of its salts show a strong blue fluorescence.

2-**Naphthylamine**-5 : 7-**disulphonic acid** :
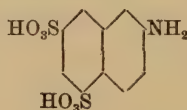
The acid crystallises with $5H_2O$ in lustrous leaflets from water and in long needles from hydrochloric acid solutions. Solutions of its salts, if pure, show a green fluorescence, but this is easily masked by the blue fluorescence of any 6 : 8-disulphonic acid present.

(2-Naphthylamine-1 : 5-disulphonic acid, when pure, shows a red fluorescence.)

The following table gives the solubilities of the acids and their salts expressed as grams of substance in 100 grams of solution at 20° :

2:5:7-*Acid.*					2:6:8-*Acid.*				
$H_2\bar{A}$	+	$5H_2O$	..	.. 23.0	$H_2\bar{A}$	+	$4H_2O$	..	.. 9.2
$Na_2\bar{A}$	+	$6H_2O$	..	.. 72.2	$Na_2\bar{A}$	+	$3H_2O$	..	.. 59.0
$NaH\bar{A}$	+	$4H_2O$	..	.. 7.9	$NaH\bar{A}$	+	$4H_2O$	..	.. 7.5
$K_2\bar{A}$	+	$2H_2O$	..	.. 63.9	$K_2\bar{A}$	+	$2H_2O$	..	.. 51.6
$KH\bar{A}$	+	$4H_2O$	..	.. 2.6	$KH\bar{A}$	+	$2H_2O$	..	.. 2.5
$Mg\bar{A}$	+	$8H_2O$	..	.. 21.1	$Mg\bar{A}$	+	$8H_2O$	..	.. 8.7
$Ca\bar{A}$	+	$4H_2O$	..	.. 40.2	$Ca\bar{A}$	+	$3H_2O$	..	.. 29.1
$Ba\bar{A}$	+	$3H_2O$	..	.. 22.7	$Ba\bar{A}$	+	$3H_2O$	..	.. 12.0

These two acids are best prepared by direct sulphonation of β-naphthylamine, as described by Fierz-David (*loc. cit.*). The naphthylamine may either be sulphonated to the disulphonic acids, when a mixture of the 6 : 8- and 5 : 7-acids, together with some 1 : 5-acid, results, these being then separated by their differences in solubility, or sulphonation may be carried further, when the 5 : 7- and 1 : 5-disulphonic acids are converted into the 1 : 5 : 7-trisulphonic acid, while the 6 : 8-disulphonic acid is unaffected. The latter method of so-called exhaustive sulphonation is preferable for the reasons already explained (p. 192). It is carried out as follows :

Finely powdered β-naphthylamine sulphate (192 gms. = 1 gm. mol.) is stirred during ten minutes into 800 gms. of 15 per cent. oleum, the temperature being kept below 50° in order to keep down the proportion of 8-monosulphonic acid formed as far as possible. Stirring is continued at about 50° until monosulphonation is complete, as shown by a test portion dissolving to a clear solution in dilute soda. This usually takes about fifteen minutes. The solution is now cooled to 40° and 350 gms. of 66 per cent. oleum added within fifteen minutes. The temperature is then maintained at 55° for a day, by which time disulphonation should be complete. On the following day, the temperature is raised to 85° slowly and kept at this point for eight hours to form the 1 : 5 : 7-trisulphonic acid. The solution is then cooled to 50° and poured with good stirring into a mixture of 800 gms. of ice-water and 1,100 gms. of ice. When all is added, the temperature of the solution should be about 60°. On cooling, and allowing to stand for six hours at 20°, the 6 : 8-disulphonic acid separates completely and is filtered off and pressed.

The filtrate is then boiled for four hours (b.p. 125°), the volume being kept up, when the 1 : 5 : 7-trisulphonic acid loses its 1-sulpho group by hydrolysis and, on cooling and allowing to stand for two days at 0°, the 5 : 7-disulphonic acid separates. It is filtered off and pressed.

The final filtrate contains about 22 gms. of sulphonic acids per litre, which are not recovered.

For purification, the press-cake of the 6 : 8-acid is dissolved in about 700 c.c. of boiling water and 70 gms. of salt added to the solution, which then sets to a solid mass of the acid sodium salt of the 6 : 8-acid. After standing for twelve hours, this is filtered off, pressed, and dried. The press-cake of the 5 : 7-acid is dissolved in five times its weight of water and precipitated as acid sodium salt with half its weight of salt.

The yield of 6 : 8-acid obtained corresponds to 30 gms. of nitrite, and that of 5 : 7-acid to 26 gms. of nitrite, or a combined yield of 81 per cent.

Another method of preparing 2-naphthylamine-6 : 8-disulphonic acid is described on p. 189, where its application as an intermediate for azo dyes is also given. 2-Naphthylamine-5 : 7-disulphonic acid is not used as a dyestuff intermediate, but serves for the preparation of J-acid (p. 195).

2-**Amino**-8-**naphthol**-6-**sulphonic acid** (Gamma-acid):
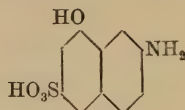
The acid forms very sparingly soluble needles. The alkali and alkaline earth salts are readily soluble. The lead salt forms sparingly soluble needles.

This acid is readily prepared from the sodium salt of 2-naphthylamine-6 : 8-disulphonic acid by heating it with concentrated caustic soda at high temperatures, usually in an autoclave (Cassella and Co., G.P. Anm. C 3063; E.P. 16699 of 1889). The disulphonate, which should be fairly free from salt, is heated with twice its weight of 50 per cent. caustic soda solution at 190° to 195° for six hours in a stirring autoclave. After cooling, the melt is diluted with water, and the solution acidified with mineral acid, when the Gamma-acid is precipitated.

The strength and purity of Gamma-acid, as with other aminonaphtholsulphonic acids (see H-acid, p. 171) are estimated by (1) coupling a weighed quantity in alkaline solution with a standard solution of a diazo compound, and (2) titrating a second sample in weak acid solution with standard nitrite solution. The two results should agree closely.

Gamma-acid can be coupled with diazo compounds in two ways : (1) in alkaline solution, when coupling takes place in the o-position to the hydroxyl group; (2) in weak acid solution, when coupling takes place in the o-position to the amino group (the 1-position). It is, therefore, capable of forming two different azo dyes with the same first component :
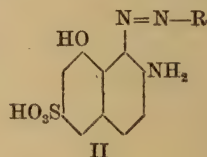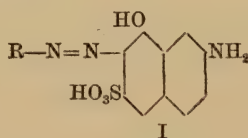
Examples of both kinds are made, generally in conjunction with diamines of the benzidine series as first components. But those of the first class (I) are the more valuable, because in them the amino group of the Gamma-acid part of the molecule can be diazotised and coupled with a new end component. This last diazotisation and coupling are usually carried out on the fibre, the original dye being said to be " developed." In this way a number of valuable blacks and browns are produced on cotton, using various developers such as m-phenylenediamine, β-naphthol, etc.

2-Phenylamino-8-**naphthol**-6-**sulphonic acid** (Phenylgamma-acid) :
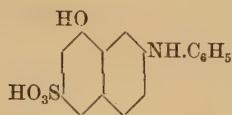
The acid is practically insoluble in water, but its salts are mostly soluble.

This substance is obtained from Gamma-acid by an application of the Bucherer reaction. According to Fierz-David ("Farbenchemie," 1920, p. 127), 224 gms. of 100 per cent. Gamma-acid is heated with 200 gms. of aniline, 750 gms. of sodium bisulphite solution (25 per cent. SO_2), and 750 c.c. of water under reflux for twenty-four hours. The solution is then made distinctly alkaline with sodium carbonate, excess aniline distilled off with steam, and the residual solution acidified with hydrochloric acid, when phenylgamma-acid is precipitated. The yield is about 270 gms. of 90 per cent. acid or a yield of 90 per cent.

The hydroxyl group is unaffected in this reaction, owing to the presence of a sulpho group in the *m*-position, in accordance with the rule elucidated by Bucherer (p. 140).

Phenylgamma-acid is used as an end component in several complex azo dyes, the coupling being effected in alkaline solution.

2-Amino-5-**naphthol**-7-**sulphonic acid** (J-acid):
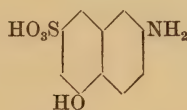
The acid forms a pale grey crystalline powder, sparingly soluble in cold water, rather more soluble in hot water. The salts are soluble, and their solutions show a blue fluorescence.

It is prepared from 2-naphthylamine-5 : 7-disulphonic acid by a method similar to that used for Gamma-acid (G.P. 75469, Badische).

Phenyl-J-acid—
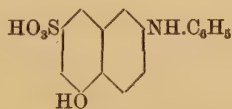
—is prepared from J-acid by the same method as that used for preparing Phenyl-gamma-acid from Gamma-acid.

J-acid resembles Gamma-acid (p. 194) in forming two sets of dyes, according to whether it is coupled with diazo compounds in alkaline or in acid solution. It is, therefore, used like Gamma-acid for the preparation of developing colours.

J-acid also possesses the remarkable property of conferring on polyazo dyes, of which it is an end component, the ability to dye cotton without the aid of a mordant. Phenyl-J-acid also possesses this property, and both intermediates are used as end

components in several trisazo dyes which, though not containing benzidine derivatives, or other diamines as first components, are direct cotton colours.

2-**Hydroxy**-3-**naphthoic acid** (β-Oxynaphthoic acid):
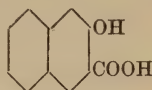
The acid crystallises in leaflets, m.p. 216°. It is almost insoluble in cold water, but is sparingly soluble in hot water, moderately in benzene and chloroform, and easily soluble in alcohol and ether. Its sodium salt is soluble in water.

This substance is prepared by the action of carbon dioxide on dry sodium β-naphtholate in the same manner as salicylic acid is prepared from sodium phenate (p. 96). Presumably sodium β-naphtholcarbonate is first formed. The temperature required for its conversion to the 3-naphthoic acid is much higher than that required for salicylic acid, being 200° to 250° (G.P. 50341, Heyden). If the naphtholcarbonate is heated at 130°, 2-hydroxy-1-naphthoic acid is formed (m.p. 156° to 157°), a very unstable substance which readily loses carbon dioxide and reverts to β-naphthol.

According to U.S.P. 1450990 (Shorey), the yield and quality of the oxynaphthoic acid are much improved by working at the upper temperature limit, 250°, since β-naphthol is formed from the naphtholate to some extent, and the presence of this is deleterious by hindering contact of carbon dioxide with the sodium compound, and by promoting the formation of more β-naphthol. By working at 250°, however, any β-naphthol formed is at once vaporised, and can be removed from the autoclave, condensed, and returned to it later. A pressure of 50 lbs. per sq. in. is maintained in the autoclave.

A method of purifying the technical product is described by Strohbach (*Ber.*, 1901, **34,** 4142).

β-Oxynaphthoic acid is used as an end component in a few monoazo colours, which are applied as lake pigments. Its main use, however, is for the preparation of its anilide and similar derivatives, of which a description follows.

2-**Hydroxy**-3-**naphthoic anilide** (Naphthol AS)—
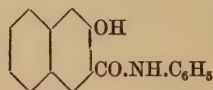
—colourless leaflets, m.p. 243° to 442°, soluble in hot glacial acetic acid and nitrobenzene, sparingly soluble in alcohol.

This is prepared by condensation of aniline with 2-hydroxy-3-naphthoic acid in an indifferent solvent, using phosphorus trichloride, phosphorus oxychloride, thionyl chloride, etc., as condensing agents. The following method is given by G.P. 293897 (Griesheim-Elektron).

A suspension of 188 parts of 2-hydroxy-3-naphthoic acid in toluene is stirred with 93 parts of aniline and 60 parts of phosphorus trichloride slowly dropped in. The mixture is then boiled under reflux until free amine is no longer present. After

making faintly alkaline with sodium carbonate, the toluene is distilled off with steam and the residual naphthoic anilide filtered off, washed, and dried.   It is obtained as a colourless powder.

Substantially the same method is described in G.P. 294799 (Meister Lucius and Brüning), where the yield of anilide is given as 91 per cent.

Other arylamides of β-oxynaphthoic acid are made in a similar manner—*e.g.*, the *m*-nitroanilide (Naphthol AS-BS), the α-naphthalide (Naphthol AS-BO), and the *p*-anisidide (Naphthol AS-RL).

Naphthol AS and the other members of this series are used in producing insoluble azo colours on cotton in much the same way as β-naphthol is used.   But they have the advantage that they possess definite affinity for cotton, so that after steeping the cotton in an alkaline solution of Naphthol AS, etc., it need only be squeezed before passing on to the solution of diazotised base.   The dyeings produced are also fuller, more level and brighter than those obtained with β-naphthol.

α-**Nitroso**-β-**naphthol**—
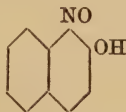
—a light yellow powder, or brownish-yellow crystals, m.p. 112°, almost insoluble in water, but soluble in organic solvents.   It is best crystallised from hot ligroin (D 0·71 to 0·72).

This substance is prepared by dissolving β-naphthol in water and the necessary amount of caustic soda so as to make approximately a 10 per cent. solution, adding a slight excess of sodium nitrite, cooling to 0°, and dropping into the well-stirred solution dilute sulphuric acid until the solution is permanently acid to Congo paper, the temperature being kept about 0°.   The nitrosonaphthol separates at once.   It is filtered off, washed acid-free with cold water, and air-dried.   The yield is almost quantitative.   The light yellow powder obtained soon darkens in colour, and the substance should be freshly prepared as required.

It is used to some extent as a dyestuff, but is chiefly applied to the preparation of 1-amino-2-naphthol-4-sulphonic acid.

1-**Amino**-2-**naphthol**-4-**sulphonic acid**:
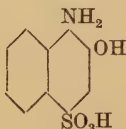
The acid crystallises in needles ($+\frac{1}{2}H_2O$), almost insoluble in cold water, and sparingly soluble in hot water.   Its sodium salt is soluble in water, and the solution quickly becomes brown in the air, owing to oxidation.

The preparation of this substance by the action of sodium bisulphite on nitroso-β-naphthol is described by Böniger (*Ber.*, 1897, **27,** 23).   The nitroso-β-naphthol first combines with bisulphite to form a soluble naphtholhydroxylaminesulphonate.   On

addition of acid to the solution, reduction and intramolecular transformation take place, with formation of the aminonaphtholsulphonic acid :
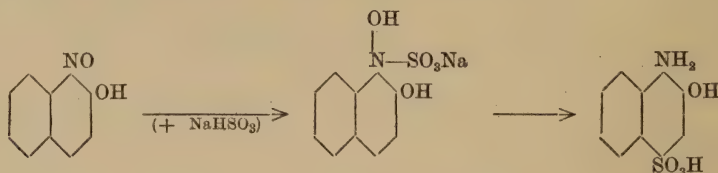
A 6 to 7 per cent. paste of 1 part of nitroso-β-naphthol is rubbed with 3 to 4 parts of cold 40 per cent. bisulphite solution. The nitroso compound quickly dissolves, except for a little resinous matter, which is removed by filtration. The solution is then warmed to 30° to 40° and 3 to 4 parts of hydrochloric acid (21° Bé) added. The solution should then be strongly mineral acid. On allowing it to stand the amino-naphtholsulphonic acid separates out, and is filtered off, washed, and dried.

1-Amino-2-naphthol-4-sulphonic acid is used as a *first* component in a number of monoazo dyes, which are, therefore, *ortho*-hydroxyazo compounds, and as such are specially suited for development on the fibre (wool) by afterchroming to produce fast black and blue-black dyeings. The diazotisation of 1-amino-2-naphthol-4-sulphonic acid requires special conditions, in particular the presence of a copper salt, since if diazotisation is carried out in the usual way internal condensation takes place with formation of a diazo-oxide, which does not couple with amines or phenols.

PHTHALIC ANHYDRIDE AND ITS DERIVATIVES

Phthalic anhydride—

$$\text{C}_6\text{H}_4\underset{-\text{CO}}{\overset{-\text{CO}}{\diagdown}}\text{O}$$
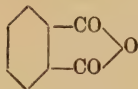
—crystallises in long white needles, m.p. 131°, b.p. 284·5°, D_4 1·527. It sublimes readily. It is sparingly soluble in water (by which it is slowly converted into phthalic acid), but is moderately soluble in alcohol, benzene, toluene, etc.

Phthalic acid forms rhombic crystals, melting at about 200°, and at the same time losing water, and being converted into the anhydride.

Phthalic anhydride is prepared by the oxidation of naphthalene, either (1) with sulphuric acid in presence of mercury as catalyst, or (2) with air, using certain metallic oxides, such as vanadium pentoxide, as catalysts.

(1) **Oxidation with Sulphuric Acid.**—This process, depending on the use of mercury as catalyst, was discovered by E. Sapper, and was patented in 1896 by the Badische Anilin- und Soda-Fabrik (G.P. 91202, E.P. 18221 of 1896). A fairly detailed description of the process has been given by Dr. H. Levinstein (*J. Soc. Dyers*, 1901, **17,** 139).

The oxidation is carried out in a shallow covered iron pan fitted with a stirrer which just scrapes the bottom, and a wide outlet pipe leading to a condenser. In this pan the mercury catalyst is first prepared by heating 4 kg. of mercury with 120 kg. of 100 per cent. sulphuric acid until all the sulphuric acid has distilled over. A previously prepared solution of 350 kg. of naphthalene in 3,675 kg. of sulphuric acid (66° Bé) and 1,050 kg. of 23 per cent. oleum is then run into the oxidation pan in portions of 22 litres and heated at 290° to 295°, so that each portion distils over in thirteen to seventeen minutes. Oxidation of the naphthalene takes place in accordance with the equation :

$$\text{C}_{10}\text{H}_8 + 9\text{SO}_3 = \text{C}_6\text{H}_4\underset{\text{CO}}{\overset{\text{CO}}{\diagdown}}\text{O} + 9\text{SO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$$
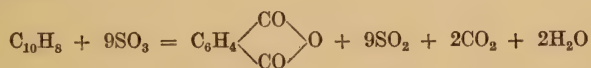
Charring also occurs to some extent, with a resulting increase in the proportion of carbon dioxide in the evolved gases. The carbon dioxide content of the gases is determined at intervals, and, when it reaches 0·6 to 0·8 per cent., the addition of naphthalene solution is interrupted. The accumulated carbon is oxidised off as far as possible by distilling a quantity of 66° Bé sulphuric acid from the pan, which is then ready for further additions of the naphthalene solution. When the carbon dioxide content reaches 1 per cent., the quantity of accumulated carbon in the pan is such that it is necessary to stop the process and clean out the pan.

In the condenser phthalic anhydride and diluted sulphuric acid collect, the sulphur dioxide being passed on to the sulphuric acid plant (contact process), where it is reoxidised to sulphur trioxide and used again. The phthalic anhydride is separated from the diluted sulphuric acid by decanting and centrifuging, and is washed free of acid. It is then dried and sublimed.

(2) **Oxidation with Air.**—The oxidation of naphthalene in the vapour phase by air in presence of catalysts has been developed into a manufacturing process in U.S.A. by Gibbs and others (original patents : U.S.P. 1285117; E.P. 119518). Manufacturing details have not been published, but an account of the laboratory experimental work is given by Conover and Gibbs (*J. Ind. Eng. Chem.*, 1922, **14,** 120) and much of the physical data required for the process is given in a series of papers in the same journal by Monroe (1919, **11,** 1116, 1119; 1920, **12,** 969).

In these experiments, hot air was passed through boiling naphthalene, and the mixture of naphthalene vapour and air passed through a tube containing the catalyst heated to a suitable temperature. The vapours leaving the catalyst were condensed, and the product worked up for phthalic anhydride. The substances found to be most active as catalysts were oxides of certain metals of the fifth and sixth periodic groups, particularly vanadium pentoxide and molybdenum trioxide.

In attempting to use oxygen alone, it was found that if the temperature rose above 300° with vanadium pentoxide as catalyst or 350° with molybdenum trioxide, ignition of the naphthalene vapour, sometimes with violent explosions, was apt to occur. On the other hand, if the temperature was kept at a safe point below these limits, only a slight amount of oxidation took place. Using air, however, the temperature could be raised to 500° without danger of ignition, and oxidation to phthalic anhydride was a maximum at about 450°.

Some typical results obtained, using vanadium pentoxide as catalyst, are given in the following table :

Naphthalene—			Anhydride Produced per Hour (*Gms.*).	Anhydride in Product (*per Cent.*).	Yield of Anhydride on $C_{10}H_8$ Attacked (*per Cent.*).
Converted (*per Cent.*).	Recovered (*per Cent.*).	Lost (*per Cent.*).			
61·9	14·5	23·6	1·24	86·9	83·5
54·8	19·0	26·2	0·99	80·6	78·5
55·6	21·7	22·7	1·15	76·0	81·8

The oxidation product contained, besides phthalic anhydride, some unchanged naphthalene, a little benzoic acid (about 1 per cent.), minute traces of naphthols, some brown matter, and substances of sharp irritating odour, these last being apparently naphthaquinones. The phthalic anhydride was isolated by fractional sublimation. Moisture and naphthalene pass over at lower temperatures than phthalic anhydride, and could be separated quite sharply. The phthalic anhydride could then be sublimed away from the brown matter, etc., which was less volatile. Another method of purification consisted in dissolving the product in carbon tetrachloride, adding a decolourising charcoal, filtering and cooling in successive stages, when the phthalic anhydride crystallised out, leaving the naphthalene in solution.

Further investigations of the oxidation of naphthalene vapour by air in presence of vanadium oxide have been made by Weiss, Downs, and Burns (*J. Ind. Eng. Chem.*, 1923, **15,** 965), and by T. Kusama (*Nippon Kwagaku Kwai Shi*, 1923, **44,** 605).

CHART XI.—DERIVATIVES OF PHTHALIC ANHYDRIDE.

The chief use of phthalic anhydride was formerly for the preparation of Indigo through anthranilic acid and phenylglycine-o-carboxylic acid, of which particulars are given later in this chapter. It is apparently still used for this purpose, but the alternative preparation of Indigo from aniline through phenylglycine (p. 65) has diminished the importance of phthalic anhydride in this connection. At the same time, increasing application has been found for it as a source of anthraquinone and its derivatives. Several examples of this are given at the end of this chapter.

As a direct intermediate for dyestuffs, it is used in the preparation of phenolphthaleïn, of the Fluorescein dyes (Eosine, Rose Bengal, etc.), and of the Rhodamines.

Dichlorophthalic anhydrides :
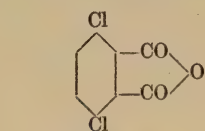
3 : 6-Dichloro-
(M.p. 191°, b.p. 339°)
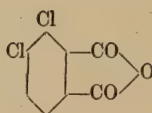
3 : 4-Dichloro-
(M.p. 120° to 121°, b.p. 329°)
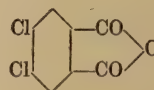
4 : 5-Dichloro-
(M.p. 185° to 187°, b.p. 313°)

A mixture of these three substances is formed when chlorine is passed through a solution of phthalic anhydride in oleum, iodine being present. The preparation is described by Villiger (*Ber.*, 1909, **42**, 3529).

A solution of 600 gms. of phthalic anhydride and 2 gms. of iodine in 3,240 gms. of 23 per cent. oleum is vigorously stirred and a slow stream of chlorine passed, while the temperature is gradually raised from 40° to 60°. The rate of passage of the chlorine is so regulated that only traces of chlorine or sulphur trioxide escape. When the increase in weight of the solution amounts to 580 gms., which requires about forty hours, the chlorsulphonic acid formed is distilled off up to 250°. The residual solution, on cooling, sets to a mass of crystals. Enough ice is carefully added to precipitate the mixed anhydrides, which are then filtered off. The mixture obtained is composed of about 50 per cent. of the 3 : 6-, 30 to 35 per cent. of the 3 : 4- and 15 to 20 per cent. of the 4 : 5-dichloro compound. For the manufacture of dyestuffs they are not separated, as they give closely similar products.

It is possible, however, to separate 3 : 6-dichlorophthalic acid from the other two compounds, owing to the insolubility of the zinc salts of the latter. The paste of mixed chloro compounds obtained, as described above, is stirred into 4 litres of hot water, which hydrolyses the anhydrides to the acids. The sulphuric acid present is precipitated by adding barium chloride, and after filtering off the barium sulphate the filtrate is exactly neutralised with sodium carbonate. The solution is then boiled out, and a concentrated solution of zinc chloride added. After heating for an hour, the precipitated zinc salts are filtered off. A solution of calcium chloride is then added to the boiling filtrate until no further precipitate of calcium 3 : 6-dichlorophthalate is formed. This is filtered off, converted into the acid by hydrochloric acid, and isolated by extraction with ether. The acid is then converted into anhydride by heating it just below its melting-point.

The 3 : 4- and 4 : 5-dichlorophthalic acids are more difficult to separate from one another.

Using a similar method of preparation, but working with 50 per cent. oleum at 60° to 70°, Pratt and Perkins (*J. Am. Chem. Soc.*, 1918, **40**, 216) obtained from 1,500 gms. of phthalic anhydride a calcium precipitate of 974 gms. and a zinc precipitate of 1,746 gms. The yields of the anhydrides, however, were much lower than would correspond with these figures.

Tetrachlorophthalic anhydride—
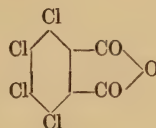
—crystallises in prisms or needles, m.p. 255° to 257°. It is insoluble in cold water, and sparingly soluble in ether. The corresponding acid crystallises with $\frac{1}{2}H_2O$, and is converted into the anhydride on heating at 109°.

The preparation is carried out by the method of Juvalta (G.P. 50177). In a cast-iron pan 10 kg. of phthalic anhydride, 30 kg. of 50 to 60 per cent. oleum and 0·5 kg. of iodine are mixed and chlorine is passed in at 50° to 60°. The chloro compound mostly separates as it is formed, causing the mass to become thick. The temperature is gradually raised to 200°, and when at this temperature all the iodine has been converted into iodine chloride, the reaction is over. Most of the chlorsulphonic acid is then distilled off, and enough ice is added to the residue to reduce the temperature to below 50°. The tetrachlorophthalic anhydride is filtered off, washed, and dried.

Dichloro- and tetrachlorophthalic anhydrides are used in the preparation of Eosin dyes (Rose Bengal, Phloxine, etc.), which are bluer in shade and more brilliant than those prepared from the unchlorinated phthalic anhydride.

Phthalimide—
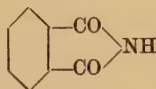
—m.p. 234°. It sublimes readily.

This is prepared from phthalic anhydride by heating with ammonia or ammonium carbonate. The former method is described by Levinstein (*J. Soc. Dyers,* 1901, **17**, 139).

In a cast-iron pan 650 parts of phthalic anhydride are melted and, while ammonia is slowly passed through, gradually raised to 140° during four hours. During the next seven to eight hours the temperature is raised to 170°. It is then raised to 240°. About 70 to 75 parts of ammonia are required, and the process lasts about eighteen hours in all. The molten phthalimide is then run off, and when cool is ground to a fine powder. The yield is 635 parts.

A convenient laboratory method is to heat 50 gms. of phthalic anhydride with 60 gms. of ammonium carbonate to 225° in a flask immersed in an oil-bath. At 100° water and carbon dioxide escape, and the mass melts. Towards the end it again

solidifies. It is then dissolved in boiling water, the solution filtered, and, on cooling, phthalimide crystallises out (Möhlau and Bucherer, " Farbenchemisches Praktikum," p. 289).

Phthalimide is used for the preparation of anthranilic acid.

Anthranilic acid :

$$\text{C}_6\text{H}_4\begin{cases}\text{COOH}\\\text{NH}_2\end{cases}$$
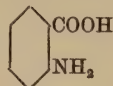
The acid crystallises in colourless leaflets, m.p. 144·6°. 100 parts of water at 13·8° dissolve 0·35 part. 100 parts of 90 per cent. alcohol at 9·6° dissolve 10·7 parts. Solutions of the acid and its salts show a blue fluorescence.

This substance is usually prepared by the action of sodium hydroxide and sodium hypochlorite on phthalimide (Hofmann transformation) :

$$\text{C}_6\text{H}_4\!\!<^{\text{CO}}_{\text{CO}}\!\!>\!\text{NH} + 3\text{NaOH} + \text{NaOCl} = \text{C}_6\text{H}_4\!\!<^{\text{COONa}}_{\text{NH}_2} + \text{Na}_2\text{CO}_3 + \text{NaCl} + \text{H}_2\text{O}$$
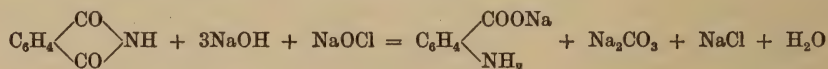
The preparation is described in G.P. 55988 (Badische): 1 part of finely powdered phthalimide is covered with a cold solution of 2 parts of caustic soda in 7 parts of water, and allowed to stand for an hour, during which the phthalimide is hydrolysed to sodium phthalamate :

$$\text{C}_6\text{H}_4\!\!<^{\text{CO.NH}_2}_{\text{COONa}}$$
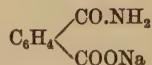
The solution is then stirred and 10 parts of hypochlorite solution, containing 5·06 per cent. NaOCl, is run in. The temperature rises to 50° to 60°. The solution is then warmed for a few minutes to 80°, at which temperature the transformation is quickly completed. After cooling, the solution is nearly neutralised with hydrochloric or dilute sulphuric acid. It is then acidified with acetic acid, when most of the anthranilic acid precipitates and is filtered off. The remainder can be precipitated from the filtrate as the insoluble copper salt by adding copper sulphate solution.

The industrial application of this method is described by Levinstein (*J. Soc. Dyers,* 1901, **17,** 139) thus: 500 parts of phthalimide are dissolved in a cold solution of 144 parts of chlorine in 640 parts of caustic soda solution (40° Bé) and 440 parts of water. The solution is filtered and, while stirring, is saturated with sulphur dioxide. On adding 600 parts of hydrochloric acid, anthranilic acid separates.

Anthranilic acid can also be prepared in good yield (80 to 85 per cent.) by oxidation of acet-*o*-toluidide with permanganate (G.PP. 119462, 94629).

Besides its application as a stage in the production of Indigo from phthalic anhydride, anthranilic acid is used as a first component in several monoazo colours, which are chiefly used as lake pigments. It is also condensed with chloroanthra-quinones to produce *o*-carboxyphenylaminoanthraquinones, which are further condensed to anthraquinoneacridone derivatives (Indanthrene Violet RN and Red Violet 2RN).

Phenylglycine-*o*-carboxylic acid :

$$C_6H_4\begin{cases}COOH \\ NH.CH_2.COOH\end{cases}$$

The acid forms a sandy powder, melting at 207° with decomposition. It is moderately soluble in hot water, alcohol, ether, and glacial acetic acid, but almost insoluble in benzene.

This substance can be prepared by the action of anthranilic acid on chloroacetic acid. In Heumann's patent (G.P. 56273), the two acids are heated together, with or without water, at about 100° for one to two hours. Under these conditions, however, some decomposition of the phenylglycine-*o*-carboxylic acid occurs. G.P. 127178, therefore, recommends the use of the sodium salts of the acids, these being heated in solution at a temperature of not over 40°, in order to avoid formation of anthranilo-diacetic acid :

$$C_6H_4\begin{cases}COOH \\ NH(CH_2.COOH)_2\end{cases}$$
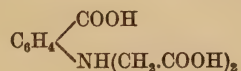
An acid sodium salt of phenylglycine-*o*-carboxylic acid is formed, which is insoluble in the cold mixture, and is filtered off. By this method the reaction takes several days to complete.

Haller (*J. Ind. Eng. Chem.*, 1922, **14**, 1040) finds that the formation of anthranilo-diacetic acid can be avoided by using excess of anthranilic acid (2 molecules of anthranilic acid to one of chloroacetic acid), and carries out the preparation as follows :

25 gms. of anthranilic acid is stirred with 150 c.c. of water, containing 22·4 gms. of sodium carbonate (2·33 mols.) and 8·6 gms. of chloroacetic acid dissolved in 50 c.c. of water added. The mixture is heated and stirred at 90° for one hour. After cooling, the solution is acidified with hydrochloric acid, and allowed to stand for twenty-four hours. The phenylglycine-*o*-carboxylic acid which separates is filtered off and washed with water. Unchanged anthranilic acid is recovered from the mother liquor by dissolving 70 gms. of sodium acetate in it and allowing the solution to stand overnight. The yield of phenylglycine-*o*-carboxylic acid is 68·6 per cent. or, allowing for the anthranilic acid recovered, 83·3 per cent.

Another method of preparation of phenylglycine-*o*-carboxylic acid, developed by H. T. Bucherer and the Badische Anilin- und Soda-Fabrik, depends on the following series of reactions :

$$(1)\quad C_6H_4\begin{cases}NH_2 \\ COONa\end{cases} + \underset{\text{Formaldehydebisulphite}}{HO.CH_2.SO_3Na} \longrightarrow C_6H_4\begin{cases}NH.CH_2.SO_3Na \\ COONa\end{cases} + H_2O$$

$$(2)\quad C_6H_4\begin{cases}NH.CH_2.SO_3Na \\ COONa\end{cases} + NaCN \longrightarrow C_6H_4\begin{cases}NH.CH_2.CN \\ COONa\end{cases} + Na_2SO_3$$

$$(3)\quad C_6H_4\begin{cases}NH.CH_2.CN \\ COONa\end{cases} + NaOH + H_2O \longrightarrow C_6H_4\begin{cases}NH.CH_2.COONa \\ COONa\end{cases} + NH_3$$
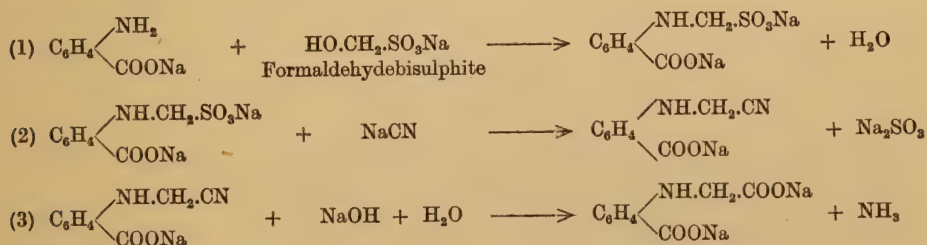
The method is described by Möhlau and Bucherer (" Farbenchemisches Prak-tikum," p. 289) :

7·5 c.c. of 40 per cent. formaldehyde solution (0·1 mol.) and 20 c.c. of sodium bisulphite solution (38° Bé, 0·1 mol.) are mixed and heated for about a quarter of an hour until the smell of formaldehyde has disappeared. To the neutral solution of sodium hydroxymethylsulphonate so formed, a concentrated solution of 15·9 gms. (0·1 mol.) of sodium anthranilate is added and the mixture heated on the water-bath until the solution no longer contains diazotisable matter. About half to three-quarters of an hour is required for this reaction. A solution of 7 gms. of potassium cyanide in 25 c.c. of water is now added and heating continued at 70° to 80° for a further quarter of an hour to form the nitrile, which can then be precipitated by acidifying with acetic acid.

The nitrile can be formed from anthranilic acid in one operation without the use of bisulphite as follows : Anthranilic acid (14 gms. = 0·1 mol.) is suspended in 50 c.c. of benzene, and 7 gms. of potassium cyanide, powdered as finely as possible, is added. 7·5 c.c. of 40 per cent. formaldehyde is then added with shaking. Much heat is developed, and the potassium salt of the nitrile is formed in the aqueous layer.

The upper benzene layer is then separated, and the syrupy aqueous solution of the nitrile treated with 20 c.c. of 40 per cent. caustic soda solution. The mixture is heated cautiously till hydrolysis sets in with vigorous evolution of ammonia. When this slackens, the solution is further boiled until the ammonia is completely driven off, the volume of the solution being maintained by addition of water. The cooled pale blue solution is carefully neutralised with concentrated hydrochloric acid, using phenolphthaleïn as indicator. It is then acidified with 15 c.c. glacial acetic acid, and after allowing to stand for some time, the phenylglycine-o-carboxylic acid is filtered off, washed, and dried.

Phenylglycine-o-carboxylic acid is used for the manufacture of Indigo.

Thiosalicylic acid—
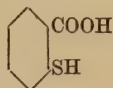
—pale yellow crystals, m.p. 164° to 165°.

This is prepared by the action of sodium disulphide on diazotised anthranilic acid and reduction of the dithiosalicylic acid so formed (G.P. 205450, Kalle and Co.) :
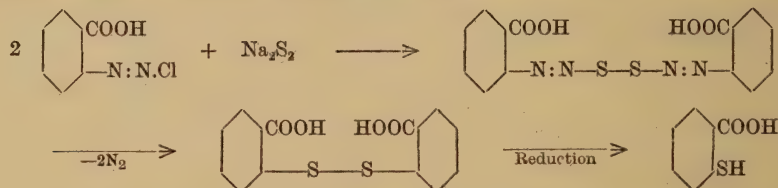
137 kg. of anthranilic acid are stirred with 500 litres of water and 240 kg. of con-centrated hydrochloric acid, ice is added, and diazotisation carried out in the usual way by running in a strong solution of 69 kg. of sodium nitrite. The diazo solution is

let flow into a well-stirred solution of 33·6 kg. of sulphur and 260 kg. of sodium sulphide in 260 litres of water, to which has been added 120 kg. of caustic soda solution (40° Bé) and 300 kg. of ice.   The temperature during addition of the diazo solution is not to exceed 5°.   Nitrogen is evolved and the temperature of the mixture rises to 15° to 25°, dithiosalicylic acid being formed.   After several hours the solution is acidified with hydrochloric acid, the precipitated dithiosalicylic acid filtered off, and washed with 1,000 litres of water.   It is then dissolved by boiling it with water and 60 kg. of soda ash, filtered from sulphur, and the filtrate boiled with 60 to 100 kg. of iron powder (or the equivalent in zinc dust) until a sample, treated with caustic soda and filtered, on acidifying no longer smells of hydrogen sulphide, but gives a precipitate easily and completely soluble in cold alcohol.   The mixture is then treated with 120 kg. of caustic soda solution (40° Bé), again boiled up, filtered from iron, etc., and the filtrate acidified with hydrochloric acid, when thiosalicylic acid is precipitated as a colourless or pale yellow precipitate.   After cooling, this is filtered off and washed.

Thiosalicylic acid is used in the preparation of phenylthioglycol-*o*-carboxylic acid.

Phenylthioglycol-*o*-carboxylic acid—

$$\text{COOH} \atop \text{S.CH}_2\text{.COOH}$$

—white crystals, m.p. 213°.

This is prepared by the action of chloroacetic acid on thiosalicylic acid, the reaction proceeding smoothly with no such side reactions as occur in making the analogous phenylglycine-*o*-carboxylic acid.

A solution of 15·4 kg. of thiosalicylic acid in water and 24 kg. of caustic soda solution (40° Bé) is treated with a solution of 9·5 kg. of chloroacetic acid in water and the necessary sodium carbonate.   The mixture is gently warmed.   On addition of acid, phenylthioglycol-*o*-carboxylic acid separates as white crystals, which are filtered off, washed, pressed, and dried (G.P. 192075, Kalle and Co.).

It is used in preparing 2-hydroxythionaphthen and its carboxylic acid.

2-Hydroxythionaphthen-1-carboxylic acid—

$$\text{C(OH)} \atop \text{S} {\searrow} \text{C.COOH}$$
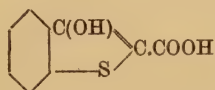
—m.p. 213°.   Sparingly soluble in cold water, more soluble in alcohol.

2-Hydroxythionaphthen (Thioindoxyl)—

$$\text{.C(OH)} \atop \text{S} {\searrow} \text{CH}$$
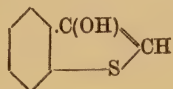
—m.p. 71°.

These two substances are readily prepared by alkali fusion of phenylthioglycol-*o*-carboxylic acid, internal condensation taking place with formation of the sodium salt of the hydroxythionaphthencarboxylic acid.   This sodium salt is fairly stable,

but on acidification the acid formed readily loses carbon dioxide to form hydroxythio-naphthen :
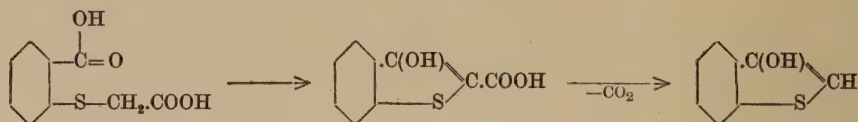
20 kg. of phenylthioglycol-*o*-carboxylic acid is stirred with a little water and added at about 100° to a mixture of 100 kg. of caustic soda and 20 litres of water.   The temperature is then raised to 170° to 180° and kept at this point for an hour.   The cooled melt is dissolved in water and made slightly acid, avoiding rise of temperature.   The precipitated hydroxythionaphthencarboxylic acid is filtered off and pressed.

To obtain hydroxythionaphthen, the acidified solution is heated until evolution of carbon dioxide ceases.   On cooling, hydroxythionaphthen crystallises out and is filtered off (G.P. 192075, Kalle and Co.).

Hydroxythionaphthen and its carboxylic acid are used in the preparation of Thioindigo Red.

Anthraquinone Derivatives from Phthalic Anhydride.

Phthalic anhydride can be condensed with various benzene derivatives to form anthraquinone derivatives either (1) directly, under the influence of a condensing agent, such as sulphuric acid or boric acid, or (2) by an application of the Friedel-Crafts reaction, using aluminium chloride, a benzoylbenzoic acid derivative is first formed, and this, when acted on by dehydrating agents, condenses internally to form an anthraquinone derivative.   Quinizarin (1 : 4-dihydroxyanthraquinone) is best prepared by the first method, while anthraquinone itself and β-methylanthraquinone are obtained by the second method.

Quinizarin—
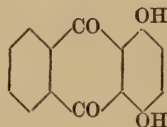
—yellowish-red leaflets or red needles, m.p. 198°, almost insoluble in water, but soluble in caustic alkalies to an intense blue-violet solution.   It is soluble in benzene and ether, the solution in the latter showing a greenish-yellow fluorescence.

The method of preparation is described in G.P. 255031 (Bayer), *p*-chlorophenol being condensed with phthalic anhydride in sulphuric acid solution, in presence of boric acid.   The chlorine atom is replaced by hydroxyl during the condensation. The action of the boric acid is not understood, but it is quite essential since, without it, the yield of quinizarin is only 4 to 5 per cent.

To 400 parts of 96 per cent. sulphuric acid are added 80 parts of phthalic anhydride, 20 parts of boric acid, and 23 parts of *p*-chlorophenol.   The mixture is heated at 150° for three hours, and is then raised to 180° to 200°, at which temperature it is kept

until the quinizarin formation is complete, as shown by the solution no longer deepening in colour. After cooling, the solution is poured into 20 parts of water, filtered, and the residue boiled up with a large proportion of water. The quinizarin is then filtered off and dried. The yield is 70 to 80 per cent.

Another method of preparing quinizarin is described on p. 231.

Quinizarin is used for the production of acid wool colours by condensation with *p*-toluidine and sulphonation of the products, when the sulpho groups enter the tolyl nuclei. Only one of the hydroxyl groups of quinizarin can be replaced conveniently by direct action of *p*-toluidine on quinizarin, and the sulphonated product constitutes Alizarin Irisol. The replacement of both hydroxyl groups by tolylamino is more easily accomplished if *leuco*quinizarin (prepared by reduction of quinizarin with sodium hydrosulphite and caustic soda) is used, and the product oxidised. The resulting dyestuff is Alizarin Cyanine Green.

Anthraquinone:
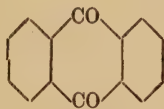
(For properties, etc., see p. 216.)

The synthesis of anthraquinone from phthalic anhydride and benzene has been described by Heller (*Zeit. angew. Chem.*, 1906, **19**, 669; *Ber.*, 1908, **41**, 3631).

A mixture of 1 kg. of phthalic anhydride, 3·5 kg. of benzene, and 1·8 kg. of aluminium chloride, is stirred in a lead-lined pan fitted with a reflux condenser, and is slowly warmed. At 30°, hydrochloric acid begins to come off, and the mass becomes thicker as the temperature rises, until eventually the stirrer is stopped. Heating is continued at 70° until evolution of hydrochloric acid ceases. The mass is then cooled, diluted with 3 to 4 parts of water, and the unchanged benzene distilled off with steam. The residue is made alkaline by gradual addition of caustic soda, and the liquid boiled for several hours to decompose the aluminium compounds into alumina, and to form the sodium salt of benzoyl-*o*-benzoic acid :
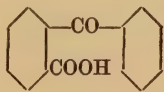
After filtering, the solution is acidified, which precipitates the benzoylbenzoic acid. The yield is 95 to 97 per cent.

This is then converted into anthraquinone by heating with 5 to 6 parts of sulphuric acid at 150° for an hour, the yield on this stage being quantitative.

β-Methylanthraquinone—
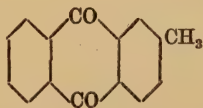
—pale yellow needles, m.p. 177°, soluble in acetic acid and benzene, but sparingly soluble in ether.

The method of preparation here is similar to that used for anthraquinone, but, as described by Heller (*loc. cit.*), differs in a few details.

Finely powdered phthalic anhydride (50 gms.) is dissolved in 200 gms. of dry toluene by heating. After cooling the solution, 75 gms. of aluminium chloride is gradually added, and the mixture stirred for five hours at the ordinary temperature. When evolution of hydrochloric acid has ceased, the mixture is warmed for an hour on the water-bath. It is then cooled, ice added, and the excess of toluene distilled off with steam. The residual liquid contains a semi-solid cake of crude toluyl-*o*-benzoic acid :
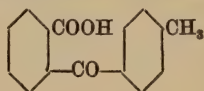
The aqueous liquid is poured off and the solid dissolved as far as possible in sodium carbonate. The filtered solution is acidified with hydrochloric acid and, after standing, the precipitated toluyl-*o*-benzoic acid is filtered off and dried. The yield is 75 gms. It is dissolved in 730 gms. of 20 per cent. oleum, and the solution warmed for one and a half hours on the water-bath. It is then poured on ice, and the filtered methylanthraquinone purified by boiling with dilute soda.

β-Methylanthraquinone is used chiefly for the preparation of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl, which readily undergoes internal condensation to pyranthrone, an orange vat dyestuff of valuable properties. For the preparation of the dimethyldianthraquinonyl two methods have been described—(1) by nitration of β-methylanthraquinone to the α-nitro derivative, reduction of this to the amino compound, diazotisation of the latter and treatment of the diazo compound with copper powder :
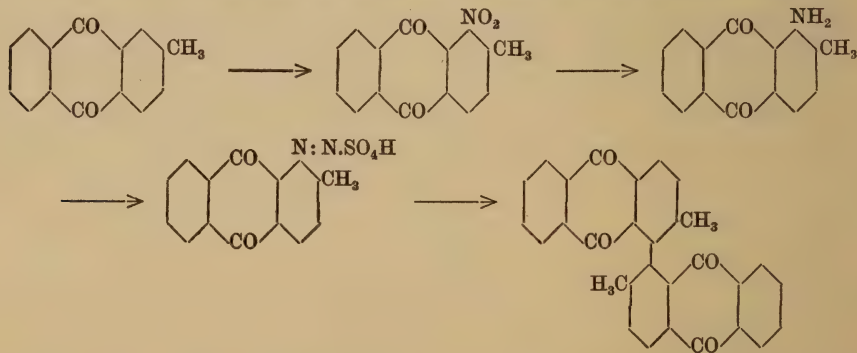
(2) by chlorination of β-methylanthraquinone to 1-chloro-2-methylanthraquinone and condensation of 2 molecules of this by copper powder in a high-boiling solvent :
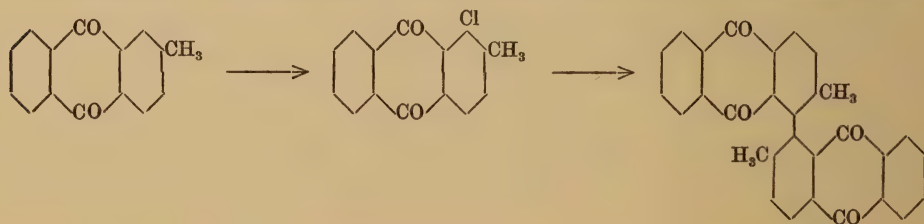
The intermediate amino- and chloro-derivatives are prepared as follows :

1-Amino-2-methylanthraquinone.—Red crystals, m.p. 202°, insoluble in water, but soluble in alcohol, ether, benzene, and glacial acetic acid.

(*a*) **Nitration** : This is described by Römer and Link (*Ber.*, 1883, **16,** 695).   To a cooled solution of 2 parts of β-methylanthraquinone in six to seven times its weight of sulphuric acid, 1 part of potassium nitrate (or the equivalent of sodium nitrate) is gradually added.   The nitro compound separates as a greenish-yellow crystalline mass which, after twenty-four hours, is poured into water and the yellow precipitate filtered off.   It is washed, and boiled with alcohol until the extract is pale yellow. It may be purified by crystallisation from glacial acetic acid, and is obtained as yellow crystals, m.p. 269° to 270°, sparingly soluble in alcohol and benzene, but soluble in xylene, nitrobenzene, and aniline.

(*b*) **Reduction** : This was effected by Römer and Link with stannous hydroxide, but sodium sulphide, the usual reducing agent for nitro compounds of the anthraquinone series, is preferable (G.P. 131873, Badische; Scholl and Holdermann, *Ber.*, 1907, **40,** 1696).

The nitro compound (1 part) is boiled with $3\frac{1}{2}$ parts of crystallised sodium sulphide and 20 parts of water for an hour.   The amino compound is obtained fairly pure in this way, but is purified if necessary by crystallisation from glacial acetic acid.

1-Chloro-2-methylanthraquinone.—Pale yellow crystals, m.p. 176°, sparingly soluble in cold alcohol, but moderately soluble in boiling alcohol, and easily soluble in benzene and toluene.

β-Methylanthraquinone in weak oleum solution can be chlorinated with chlorine gas (E.P. 207840, Thomas and Scottish Dyes).   It is, of course, advantageous in this case to start with toluyl-*o*-benzoic acid (p. 210), and effect the condensation to methylanthraquinone and chlorination of the latter in one operation.

35 parts of toluyl-*o*-benzoic acid is heated with 350 parts of 5 per cent. oleum in the usual way to form β-methylanthraquinone (p. 210).   This condensation being complete, 0·35 part of iodine is added, and dry chlorine is passed through the solution at 50° to 60° until the required increase in weight is attained, allowing for the solubility of chlorine in oleum.   A more efficient control of the reaction is obtained by drawing samples from time to time, and taking the melting-point of the isolated product.   When the melting-point falls below 150°, the chlorine is slowed off and the percentage of chlorine in the subsequent samples determined.   When the chlorine content reaches 13·8 to 14·0 per cent., the passage of chlorine is stopped.   The melting-point of the sample at this stage is usually 140° to 149°.   By pouring the solution into ice, the chloromethylanthraquinone is precipitated, and can be isolated in the usual way.

Another method of chlorinating β-methylanthraquinone, by sulphuryl chloride in presence of iodine as catalyst, is described in G.P. 269249 (A.G.F.A.).

A mixture of 3 parts of β-methylanthraquinone, 5 parts of nitrobenzene, 0·2 part of iodine, and 3 to 4 parts of sulphuryl chloride is heated on the water-bath under reflux.   Sulphur dioxide and hydrochloric acid are evolved, and the reaction is complete in eight to ten hours.   After distilling off any unchanged sulphuryl chloride,

on cooling the chloromethylanthraquinone separates in star-shaped needles, which are filtered off. A further quantity can be obtained from the mother liquor by dilution with alcohol.

1-**Chloroanthraquinone**-2-**carboxylic acid** :
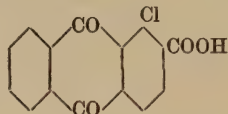
The preparation of this substance is described in the above-mentioned patent of Thomas and Scottish Dyes.

Instead of isolating the chloromethylanthraquinone, the solution is cooled, and 350 parts of sulphuric acid added. Water is then slowly added until the acid strength is about 80 per cent. This precipitates some chloromethylanthraquinone. Finely powdered manganese dioxide (95 parts) is now added, and the mixture heated to 110°, at which point it is kept for some hours. When oxidation is complete, the solution is run into water. If any unchanged manganese dioxide is left, this is removed by adding bisulphite solution and boiling up. The solution is then cooled and the carboxylic acid filtered off. It can be purified by solution in dilute alkali and reprecipitation with acid. The yield obtained (from 35 parts of toluyl-o-benzoic acid) is 30 to 32 parts.

1-Chloroanthraquinone-2-carboxylic acid is used in preparing a red vat dye, Indanthrene Red BN, by condensing it with β-naphthylamine, and further condensing the product to an acridone derivative :
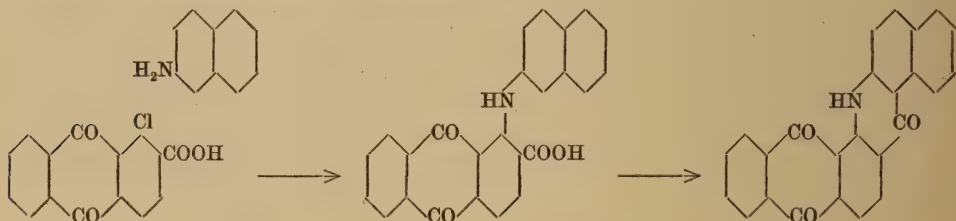
ANTHRACENE AND ANTHRAQUINONE DERIVATIVES

Anthracene—
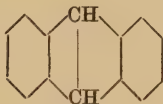
—crystallises in white tables, showing a blue-violet fluorescence; m.p. 218°, b.p. 340°; insoluble in water, sparingly soluble in alcohol; solubility at 15·5° in benzene 1·04 per cent., in acetone 0·55 per cent., in light pyridine 0·85 per cent. Solutions of anthracene, on standing in sunlight, deposit a polymeride, para-anthracene, $(C_{14}H_{10})_2$, which melts at 244°, passing at the same time back into anthracene.

Anthracene is obtained from the solid which separates on allowing the fraction of coal tar distilling between 270° and 400° to stand for several days. This solid is separated from the residual oil by the centrifuge and by hot pressing. It then contains 40 to 45 per cent. of anthracene associated mainly with carbazole and phenanthrene. Various processes are used, or have been proposed, for its purification. The most convenient seems to be that which depends on successive treatments with pyridine bases, since the solubility of carbazole at the ordinary temperature in that solvent is about 12 per cent., and that of phenanthrene about 25 per cent. The crude anthracene is heated up with a few times its weight of pyridine bases to about 100°, when the whole dissolves, and, on cooling, almost all the anthracene crystallises out. It is separated by the centrifuge, and the pyridine treatment repeated. In regular operation of this process, fresh pyridine is used for the second treatment, while for the first treatment the mother liquor from the second treatment is used. In this way a product containing about 90 per cent. of anthracene is obtained. This is further purified to a slight extent by subliming with steam at 200°, and this operation also has the advantage of converting the anthracene into a finely divided form well adapted for subsequent conversion to anthraquinone.

Special attention has been given in recent years to processes in which purification of the anthracene is combined with separation of pure carbazole. Thus Kinzlberger and Co. (E.P. 144648 and 144656) heat crude anthracene with coal-tar naphtha and 80 per cent. caustic potash for several hours at 120°. The naphtha solution of anthracene, etc., is drawn off from the solid potassium carbazole compound, and the anthracene crystallises out on cooling. Again, A. Kagan (E.P. 172864) first partly purifies the crude anthracene by crystallisation from hot cresols, followed by washing with petrol ether. The anthracene is then recrystallised from pyridine, carbazole being obtained from the mother liquor by distilling off the pyridine and recrystallising the residue from toluene, followed by sublimation. Crude anthracene of 46 per cent. strength treated in this way is said to give an 89 per cent. anthracene and a carbazole of 96 to 98 per cent. purity.

Anthracene is used almost entirely for the preparation of anthraquinone, but a vat dye of subsidiary importance, Indanthrene Olive G, is also made from it.

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Substitution Products of Anthracene.

Very little information has been published regarding the substitution products of anthracene, such as the anthracene sulphonic acids and chloroanthracenes. But these have evidently been studied technically to some extent with a view to their use in the preparation of the corresponding anthraquinone derivatives, in order to evade certain difficulties in the direct preparation of the latter from anthraquinone. It is of interest, therefore, to note such few and vague details as are available.

Chloroanthracenes.—When chlorine is passed into a solution or suspension of anthracene in a neutral organic solvent at ordinary temperature, *meso*-dichloro-anthracene—
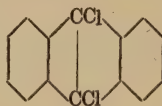
—is formed, and is isolated as yellow needles, melting at 209°, and easily soluble in benzene, but sparingly in alcohol and ether. The same compound is obtained by warming a suspension of anthracene in carbon disulphide with sulphur chloride (S_2Cl_2) until the evolution of hydrochloric acid ceases (Lippman and Pollak, *Ber.*, **34**, 2786).

With chlorine at higher temperatures various mixtures of addition and substitution products are obtained.

Anthracene Sulphonic Acids.—Anthracene is easily sulphonated by ordinary concentrated sulphuric acid to mixtures of mono- and disulphonic acids, which are not easily separated. But, by using sulphuric acid of 67 per cent. strength (53° Bé), according to G.P. 72226, the β-monosulphonic acid is obtained :
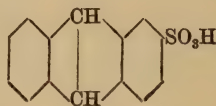
100 kg. of anthracene is stirred with 200 kg. of 67 per cent. sulphuric acid at 120° to 135° till a test shows almost complete disappearance of the anthracene. The solution is then diluted with 1,000 litres of water, neutralised with soda, and left to crystallise, when the sodium salt of the β-sulphonic acid separates in greenish iridescent masses. It may be purified by recrystallisation from hot water.

Another method of sulphonation, leading to a mixture of the α-and β-monosulphonic acids is described in G.P. 251695 (Bayer): 300 parts of anthracene are dissolved in 600 parts of glacial acetic acid. To the well-cooled solution 200 parts of chlorsulphonic acid are added slowly. When this has all been added, the mixture is quickly heated to 95°, and kept at this temperature for five hours. A clear, light olive solution is obtained. This is poured into 5,000 parts of water, and the sulphonic acids salted out and filtered off. The product is dissolved as far as possible in 4,500 parts of boiling water, cooled to 40°, and filtered. The filtrate contains the

CHART XII.—DERIVATIVES OF ANTHRACENE.

α-sulphonate, which can be salted out with 120 parts of salt. From the residue the less soluble β-sulphonate can be boiled out with a large volume of water. The yield is given as 50 per cent. of the α-sulphonate, and 30 per cent. of the β-sulphonate.

meso-**Dichloroanthracenesulphonic Acids:**

(*a*) **The β-monosulphonic acid**—
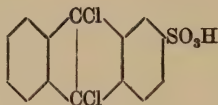
—is described in G.P. 260562 (Badische) as a yellow powder, somewhat soluble in water, the solutions having a blue fluorescence. It is obtained when dichloro-anthracene (1 part) is stirred into chloroform (100 parts) and chlorsulphonic acid added slowly at 30°, the solution being afterwards kept at 40° for four hours. The same sulphonic acid is said to be produced when oleum is used in place of chlorsul-phonic acid.

This *meso*-dichloroanthracene-β-sulphonic acid is used to prepare β-**aminoanthra-quinone** as follows (G.P. 288996): 100 parts of a 50 per cent. paste of the acid are heated with 60 parts of copper oxide and 600 parts of 25 per cent. ammonia solution in a stirred autoclave for twenty-four hours at 200°. The crude β-aminoanthra-quinone is filtered off and the copper, etc., removed by extraction with dilute nitric acid or by recrystallisation of the product from nitrobenzene or other suitable solvent. A particularly pure β-aminoanthraquinone is said to be obtained in this way. Other oxidising agents, such as manganese dioxide, may be used in place of copper oxide.

(*b*) *meso*-**Dichloroanthracene**-2 : 6 **and** 2 : 7-**disulphonic acids** are apparently obtained by sulphonating *meso*-dichloroanthracene, but no information is available as to how this is carried out.

The 2 : 7-acid yields 2 : 7-dichloroanthraquinone when acted on by sodium chlorate and hydrochloric acid (G.P. 228876). 60 kg. of the sodium salt of dichloro-anthracene-2 : 7-disulphonic acid are dissolved in 1,000 litres of water, and 100 kg. of hydrochloric acid (20° Bé) are added, followed by a solution of 50 to 100 kg. of sodium chlorate in 750 litres of water. The solution is heated for twenty-four hours at about 100°. The 2 : 7-dichloroanthraquinone precipitates in pure condition.

Anthraquinone—
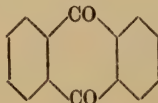
—very pale yellow needles, m.p. 284·6°, b.p. 382°. It is insoluble in water, and sparingly soluble in most organic solvents. Glacial acetic acid and nitrobenzene dissolve it fairly well when hot, and it can be conveniently crystallised from these solvents. It also dissolves readily in concentrated sulphuric acid, which does not sulphonate it even when hot; the anthraquinone is precipitated unchanged on dilution.

A characteristic reaction is the formation of a red solution, of the sodium derivative of oxanthranol—

$$C_6H_4 \underset{C(OH)}{\overset{C(OH)}{\diagup \diagdown}} C_6H_4$$
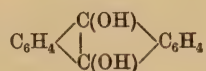
—on reduction with hydrosulphite and alkali.

I. Preparation from Anthracene.

Anthracene can be oxidised to anthraquinone in various ways, of which the best established and the one used industrially is oxidation with chromic acid. Formerly a very crude anthracene was used as starting material, but the tendency now is to employ as pure an anthracene as possible, certainly one of over 90 per cent. strength, obtained in some such manner as that described above.

(a) **Oxidation with Chromic Acid.**—The anthracene is oxidised according to the equation :

$$C_{14}H_{10} + Na_2Cr_2O_7 + 4H_2SO_4 = C_{14}H_8O_2 + Na_2SO_4 + Cr_2(SO_4)_3 + 5H_2O$$
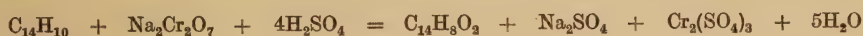
Any phenanthrene present is oxidised to phenanthraquinone. Other impurities mostly oxidise to carbon dioxide and water. The quantity of dichromate required will naturally depend on the proportion of impurities present.

150 parts of purified sublimed anthracene are stirred into 3,000 parts of water in a lead-lined vessel. 300 parts of sodium dichromate are added, and the solution heated to 80°. 900 parts of 50 per cent. sulphuric acid are then slowly run in over ten to twelve hours, the temperature at the same time being raised to the boiling-point. Some frothing occurs owing to evolution of carbon dioxide, and if the anthracene used is very impure, it may be necessary to work at greater dilution and to add the acid more slowly. After the acid has all been added, the mixture is boiled for some time to complete the oxidation. The progress of the oxidation is tested by filtering and washing a sample and then subliming the solid. Unchanged anthracene appears in the sublimate as silvery leaflets, while anthraquinone forms sharp needles. The solution is also tested from time to time for the presence of chromic acid.

When oxidation is complete, the reaction mixture is filtered, well washed with water, and dried. (On the manufacturing scale the filtrate is either worked up for chromic sulphate, which is sold to the tanners, or the chromic salt is reoxidised to dichromate. This recovery of the chromium compounds is an important economic feature of the process.) The crude anthraquinone is now partly purified by heating it with two and a half times its weight of 80 per cent. sulphuric acid at 120° for a few hours, which sulphonates any unchanged anthracene and some other impurities which may be present. The solution is then poured into water and the precipitated anthraquinone filtered off, washed, and dried. A final purification is obtained by subliming the product with superheated steam at 240° to 260°. The yield obtained is 106 parts of anthraquinone from 100 parts of anthracene or about 90 per cent. The loss is chiefly due to unoxidised anthracene. For the purpose of estimating the yield, the

anthracene content of the starting material is determined by the Luck method (Lunge, " Technical Methods of Analysis," Vol. II., p. 805).

(b) **Oxidation with Nitrogen Oxides.**—A number of patents have been taken out for the use of oxides of nitrogen or of nitric acid in the oxidation of anthracene [G.P. 215335, 234289 (E.P. 16312, 1909), 254710, 256623, 268049 (E.P. 11472, 1910)].

(c) **Use of Oxygen and a Catalyst or Oxygen Carrier.**—The *Chemische Fabrik Worms Akt. Gesell.*, in a series of recent patents (E.P. 156215, 156538, 156540, 169145), describe the oxidation of anthracene by oxygen containing a little nitrogen peroxide. For example, in the first patent, 100 kg. of anthracene are mixed with 500 to 1,000 kg. of acetic acid and a small proportion of fuming nitric acid. The mixture is heated to 80° to 90° and oxygen is forced in under pressure. Absorption is rapid and oxidation is complete in three to five hours. According to E.P. 156540, the acetic acid solvent may be diluted considerably with other (inactive) solvents, such as water, nitrobenzene, or dichlorobenzene. If acetic acid diluted with 20 per cent. of water is used, the yield of anthraquinone is 95 to 98 per cent. with a purity of 92 to 95 per cent. However, a purer product is obtained if water is excluded, and the water formed in the oxidation is taken up by a suitable agent, such as acetic anhydride, and if also sodium nitrite is substituted for the fuming nitric acid (E.P. 156538). In this case, a 95 per cent. yield of anthraquinone of 99 to 100 per cent. purity is claimed.

Other catalytic methods are described in G.P. 292681 and U.S.P. 1285117 (E.P. 119518, 1917).

II. Synthetic Method.

This is described on p. 209.

Sulphonation of Anthraquinone.

The great majority of the useful derivatives of anthraquinone are obtained, as the chart on p. 215 indicates, through the sulphonic acids, and the sulphonation of anthraquinone is, therefore, the most important fundamental operation in the preparation of the anthraquinone intermediates. In contrast with anthracene, which is easily sulphonated at comparatively low temperatures by weak sulphuric acids, anthraquinone is unattacked by 96 per cent. sulphuric acid even at 100°, though sulphonation begins at 200°. Oleum of 20 per cent. SO_3 content and upwards is required for the sulphonation of anthraquinone at more convenient temperatures. When the sulphonation is carried out in the ordinary manner, β-sulphonic acids only are formed—namely, the 2-monosulphonic acid and the 2 : 6- and 2 : 7-disulphonic acids. For long these were the only anthraquinonesulphonic acids known until the discovery, made simultaneously in 1903 by Iljinskij and Schmidt, that sulphonation in presence of a little mercury salt yielded α-sulphonic acids—that is, the 1-monosulphonic acid and the 1 : 5- and 1 : 8-disulphonic acids (but not the 1 : 4-acid). This discovery was of the greatest importance for the development of dyestuffs of the anthraquinone series, since the α-derivatives are, in general, more reactive and more deeply coloured than the β-derivatives. The β-sulphonic acids will be dealt with first.

Anthraquinone-β-sulphonic acid :

The acid forms white leaflets, soluble in water and in alcohol, but insoluble in ether. The sodium salt, $C_{14}H_7O_2.SO_3Na,H_2O$, forms silvery leaflets (it is commonly known as " silver salt "), sparingly soluble in cold water, and insoluble in caustic soda solution and in alcohol.

It has not been found possible to conduct the sulphonation of anthraquinone in such a way that only monosulphonic acid is produced. If the anthraquinone is completely sulphonated, substantial quantities of disulphonic acids are formed. In order to avoid this formation of disulphonic acids as far as possible, the sulphonation is stopped when about 75 to 80 per cent. of the anthraquinone has been attacked. This is achieved by arranging the quantity and strength of the oleum used, so that when most of the anthraquinone has been sulphonated, the oleum will have been reduced to monohydrate strength and sulphonation will stop.

208 parts of finely divided anthraquinone are stirred into 320 parts of 25 per cent. oleum or a quantity of stronger oleum containing an equal amount of free SO_3. The temperature is raised slowly, over several hours, to 140°, and kept at this point for eight hours. The melt is then cooled, poured into 6,000 parts of water, and the unchanged anthraquinone (about 50 to 80 parts) filtered off. The β-sulphonic acid may now be separated by neutralising the filtrate with chalk, filtering off the calcium sulphate, converting the calcium sulphonate into sodium salt by careful addition of soda, filtering from calcium carbonate, and evaporating to the crystallising point, when the sodium salt separates on long standing as silvery crystals.

But, according to Crossley (*J. Am. Chem. Soc.*, 1915, **37**, 2178), in this method much of the calcium salt remains adhering to the calcium sulphate and is lost. He obtains better yields by neutralising the acid solution with caustic soda and concentrating. The manufacturing method is to neutralise about three-eighths of the acid by soda ash, when part of the sodium salt separates, and is filtered off. The filtrate is then evaporated under reduced pressure until it reaches a specific gravity of 1·18 (measured hot). It is allowed to stand, when the main portion of the sodium salt crystallises out. This is filtered off and washed with salt solution. The yield of sodium salt is 140 to 200 parts, depending on the extent to which the anthraquinone is sulphonated.

The necessity for leaving some of the anthraquinone unsulphonated is, of course, a weakness and a source of trouble in the above process. The anthraquinone recovered is in a slimy condition difficult to filter and to wash free of sulphonic acids. A recent American patent, U.S.P. 1474507, suggests a method of overcoming this difficulty. When sulphonation has proceeded as far as required, sufficient concentrated sulphuric acid is added to the hot melt to make the ratio of H_2SO_4 to dissolved (unsulphonated) anthraquinone about 3 : 1, keeping the temperature about 100° to 110°. The solubility of anthraquinone in 100 per cent. H_2SO_4 at this temperature is about 35 per

cent., while in 85 per cent. H_2SO_4 the solubility is 1·3 per cent. Water is, therefore, added slowly during two hours, keeping the temperature about 110°, until the strength of the sulphuric acid has fallen to 75 per cent., and stirring is continued at this temperature until separation of the anthraquinone is complete. Under these conditions it separates in a crystalline form which, after drowning the charge in water, is easily filtered and washed acid-free.

The mother liquors contain about 2 per cent. of disulphonic acids—namely, the 2 : 6- and 2 : 7-acids.

Anthraquinone-2-sulphonic acid is used in preparing alizarin, β-aminoanthraquinone, and β-chloroanthraquinone.

Anthraquinone-2 : 6- **and** 2 : 7-**disulphonic acids:**
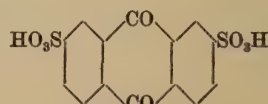
(The 2 : 6-acid is sometimes referred to as the α-disulphonic acid, and the 2 : 7- as the β-disulphonic acid, these names being survivals from the time when the constitutions of these acids were unknown.)

The 2 : 6-acid forms small yellow crystals, the 2 : 7-acid beautiful yellow plates. Both acids are soluble in water and alcohol, but insoluble in ether and benzene. Generally the salts of the 2 : 6-acid are sparingly soluble and not easily crystallised, while those of the 2 : 7-acid are easily soluble and crystallise well. The sodium salt of the 2 : 6-acid crystallises with $7H_2O$, that of the 2 : 7-acid with $4H_2O$.

The sulphonation is usually carried out by heating 100 parts of anthraquinone with 200 to 300 parts of 45 to 50 per cent. oleum at 160° to 170° till a test portion dissolves clear in water, and then continuing the heating for an hour longer in order to convert any monosulphonic acid present into disulphonic acid. These conditions favour the formation of the 2 : 6-acid. If a lower temperature is used, more of the 2 : 7 acid is obtained.

The melt is now poured into water and the solution neutralised by caustic soda. On concentrating the solution a point is reached at which, on cooling, almost all the sodium salt of the 2 : 6-acid separates as a bluish-grey crystalline precipitate, while the 2 : 7-salt and sodium sulphate remain in solution. The latter can be precipitated by alcohol, filtered off, and the 2 : 7-salt obtained by evaporating the filtrate to dryness (Crossley, *J. Am. Chem. Soc.*, 1915, **37**, 2178).

The 2 : 6-acid is used for making Flavopurpurin, and the 2 : 7-acid for Anthrapurpurin. The corresponding diamino compounds are also made from the acids.

2-**Aminoanthraquinone**—
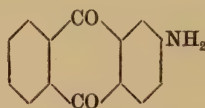
—orange-red needles, m.p. 302°. Insoluble in water; soluble in chlorobenzene and nitrobenzene, from which solvents it crystallises well. Its salts with the mineral

acids are dissociated by water. It dissolves in concentrated sulphuric acid to a yellow solution. Acetyl derivative, yellow, m.p. 262°.

2-Aminoanthraquinone is prepared by the action of ammonia at a high temperature on anthraquinone-2-sulphonic acid or, rather, its sodium salt, the reaction proceeding according to the equation :

$$C_{14}H_7O_2.SO_3Na \quad + \quad 2NH_3 \quad = \quad C_{14}H_7O_2.NH_2 \quad + \quad Na(NH_4)SO_3$$
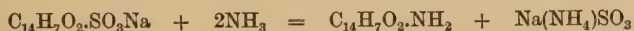
The yields obtained, however, by the use of ammonia alone are usually about 50 per cent. This is ascribed to the reducing action of the sulphite produced on the yet unchanged sulphonate, and various improvements have been proposed which are based on this theory of the course of the reaction.

(1) In G.P. 256515 (Badische), an oxidising agent is added. 250 parts of a 50 per cent. paste of sodium anthraquinone-β-sulphonate are stirred with 156 parts of 80 per cent. manganese dioxide and 130 parts of water in an autoclave. 580 parts of 25 per cent. ammonia are added, and the mixture is heated at 200° for twenty-four hours. The β-aminoanthraquinone formed is freed from manganese dioxide by treatment with sulphurous acid or sodium bisulphite. The melting-point of the product is given as about 300°, and the yield nearly quantitative.

Sodium dichromate may be used as oxidising agent in place of manganese dioxide.

(2) The addition of a salt of a metal which forms an insoluble sulphite is proposed in G.P. 267212 (Meister Lucius and Brüning). Barium chloride or the barium salt of the β-sulphonic acid is preferred, the preparation being carried out as follows : 4·12 kg. of finely powdered sodium anthraquinone-β-sulphonate are added to a solution of 2·36 kg. of crystalline barium chloride in 3·1 times its weight of water. 20·5 litres of aqueous 25 per cent. ammonia are then added, and the mixture heated for forty-eight hours at 170° to 177°, the pressure developed being 21 to 22 atmospheres. After cooling, the β-aminoanthraquinone is filtered off, and is purified by successive extractions with boiling water, dilute acid, and dilute soda. It is finally crystallised from chlorobenzene. The yield is 2·19 kg. or 73·7 per cent.

Whether the improved yield obtained by the use of barium chloride is dependent on the formation of insoluble barium sulphite during the reaction is rendered doubtful by some results given in a recent patent (G.P. 347683) of the firm of Geigy. It was found that, although calcium sulphite is insoluble, no improvement in yield was obtained by using calcium chloride. At the same time, however, it was observed that calcium chloride in conjunction with certain other inorganic salts, in particular ammonium chloride, sodium chloride, or magnesium chloride, did give an improved yield of β-aminoanthraquinone, and that, in fact, the use of calcium chloride along with magnesium chloride resulted in a better yield than could be obtained with barium chloride—namely, 80 per cent.

β-aminoanthraquinone can also be prepared from β-chloroanthraquinone (p. 222), and from meso-dichloroanthracenesulphonic acid (p. 216).

The chief uses of β-aminoanthraquinone are in the preparation of Indanthrene Blue and Flavanthrene.

2-**Chloroanthraquinone—**
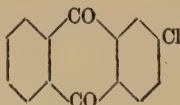
—very pale yellow crystals, m.p. 210°.   Insoluble in water.

Its preparation is described in G.P. 205195 as follows : 20 kg. of sodium anthra-quinone-β-sulphonate are dissolved in 600 litres of water and 60 litres of hydrochloric acid (20° Bé) at 100°.   A solution of 20 kg. of sodium chlorate in 200 litres of water is slowly added, keeping the temperature at 100°, until no further separation of β-chloro-anthraquinone takes place.   The chloro compound is filtered off and washed.

β-Chloroanthraquinone is used for condensations with α-aminoanthraquinones to produce αβ-dianthrimides and trianthrimides, which possess better dyeing properties than the corresponding αα-dianthrimides.   It has also been proposed to make Alizarin from β-chloroanthraquinone by fusion with caustic alkali and an oxidising agent. Lastly, β-aminoanthraquinone may be prepared from it.

β-Aminoanthraquinone from β-Chloroanthraquinone.—According to G.P. 295624 (Badische), the preparation is carried out by heating together 250 parts of β-chloro-anthraquinone, 4,000 parts of 20 per cent. ammonia, and 8 parts of crystalline copper sulphate in a stirring autoclave at 200° for twenty-six hours.   The β-amino compound separates in a pure condition, and is simply filtered off and washed. The yield is nearly quantitative.   In absence of the copper salt, the amidation of the chloro body is not complete.

Anthraquinone-α-sulphonic acid :
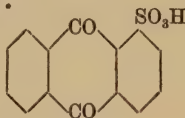
The acid forms colourless leaflets, m.p. 214°, soluble in water.   The potassium salt forms straw-yellow leaflets, and is sparingly soluble even in hot water.   The calcium salt crystallises in needles, and is moderately soluble in hot water.   The barium, strontium, and lead salts are almost insoluble in boiling water.   The aniline salt forms pale yellow needles, m.p. 291°.   The sulphochloride, $C_{14}H_7O_2.SO_2Cl$, crystallises from nitrobenzene or toluene in golden yellow prisms, m.p. 218°.

As already mentioned, anthraquinone can be sulphonated almost exclusively in the α-position if the sulphonation is carried out in presence of a trace of mercury salt (Iljinskij, *Ber.*, 1903, **36**, 4194; E.P. 10242 [1903].   R. E. Schmidt, *Ber.*, 1904, **37**, 66; G.P. 149801, E.P. 13803 of 1903).   The following process is founded on that of Schmidt, with modifications due to Fierz-David ("Farbenchemie," second edition, 1923, p. 179).

208 gms. of anthraquinone are added with stirring to 300 gms. of 18 per cent. oleum, and immediately followed by 5 gms. of finely powdered yellow mercuric oxide. (It is necessary that the mercuric oxide should be finely divided because the mercuric sulphate formed from it is surprisingly insoluble in sulphuric acid, and a thorough distribution of the mercury salt must be obtained so that it may be given every chance

to exert its directing effect, or the subsequent sulphonation will take place in the β-position.) The mixture is now stirred for an hour at 50°, then a further hour at 120°. Then 50 gms. of 60 per cent. oleum is added drop by drop within a quarter of an hour, the temperature being maintained at 120° for another one and a half hours. These quantities and conditions are such that part of the anthraquinone is left unsulphonated, in order to avoid as far as possible the formation of disulphonic acids. The melt is now poured into a mixture of 2,000 c.c. of water and 1,000 gms. of ice. The unattacked anthraquinone separates, and is filtered off (about 55 gms.). To the filtrate is added 70 gms. of potassium chloride, after which the potassium salt separates gradually. It is obtained in good crystalline form by stirring the solution for several hours at 60°. It is then filtered off, washed with a little water, and dried. The yield is 170 gms. of potassium salt, or 70 per cent., calculated on the sulphonated anthraquinone.

The mother liquor contains a few grams more of the α-sulphonate, together with some 1 : 5- and 1 : 8-disulphonates and very little of the β-sulphonate if the sulphonation has been properly carried out.

Anthraquinone-1 : 5- and 1 : 8-disulphonic acids:
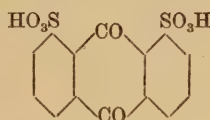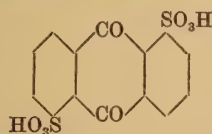
The conditions for the preparation of these acids are similar to those for the α-sulphonic acid, but stronger oleum and a higher temperature are used.

100 parts of anthraquinone are intimately mixed with 1 part of mercurous sulphate (or yellow mercuric oxide), and the mixture stirred into 200 parts of 44 per cent. oleum. The solution is slowly heated. At about 130° to 140° a reaction begins with evolution of heat. The temperature is so regulated as not to rise above 150° to 160°, and is maintained at this point until a test portion of the liquid is found to be completely soluble in water. Heating is continued further until the free SO_3 has disappeared. Meanwhile, the 1 : 5-disulphonic acid has begun to crystallise out. The melt is now cooled to 50° and 75 parts of sulphuric acid (60° Bé or 78 per cent.) added, which completes the separation of the 1 : 5-acid. This is filtered off through asbestos, and is purified by dissolving it in hot water and salting out as the potassium salt by means of potassium chloride. The acid filtrate from the 1 : 5-acid is run into water, and to the hot solution sufficient potassium chloride solution is added to form the potassium 1 : 8-disulphonate. On cooling, this separates as pale yellow needles (G.P. 157123, E.P. 13808 of 1903; *cf.* also E.P. 10242 of 1903).

The chart at the beginning of this chapter indicates sufficiently the number and variety of the derivatives obtained from the α-sulphonic acids. Those obtained from the α-monosulphonic acid will be dealt with first.

α-Aminoanthraquinone—
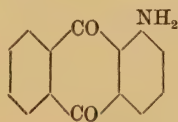
—dark red prisms with metallic reflex, most conveniently crystallised from xylene. The melting-point of the pure substance is variously stated as 241° (Fierz-David), 243° (Ullmann), and 252° (Beisler and Jones, *J. Am. Chem. Soc.*, 1922, **44**, 2299). The last-named figure is probably correct.

In G.P. 273810 (Meister Lucius and Brüning), the preparation of α-aminoanthraquinone is described, following a method similar to that used for the β-compound. 300 parts of potassium anthraquinone-α-sulphonate are stirred into 2,700 parts of 25 per cent. ammonia and 300 parts of water, 225 parts of crystalline barium chloride are added, and the mixture is heated in an autoclave at 180° to 186° for twenty hours. The α-aminoanthraquinone is filtered off and washed with alkali to remove certain by-products. It is then boiled with dilute hydrochloric acid to decompose the barium sulphite, filtered, washed, and dried. The yield of α-aminoanthraquinone is 90 per cent.

A more recent patent, E.P. 169667 (1921, *S.C.I.*, Basle), proposes to use an aromatic nitro compound as oxidising agent to deal with the sulphite produced. 165 parts of potassium anthraquinone-α-suphonate, 500 parts of 24 per cent. ammonia, and 60 parts of sodium nitrobenzene-*m*-sulphonate are heated together at 160° to 165° for twelve hours. Pure crystalline α-aminoanthraquinone separates in 80 per cent. yield. Metanilic acid is recovered from the filtrate.

Other methods available for the preparation of α-aminoanthraquinone are (1) the reduction of α-nitroanthraquinone (p. 235), and (2) the amidation of α-chloroanthra-quinone (p. 229).

While α-aminoanthraquinone is used in the production of a few vat dyes of the dianthrimide and trianthrimide types obtained by condensation with chloroanthra-quinones, it also serves as the starting material for a number of other intermediates, as indicated in the chart.

α-**Acetylaminoanthraquinone** can be prepared in the usual way by warming the amino compound with acetic anhydride. Another method is described in G.P. 211958. 10 parts of α-aminoanthraquinone are dissolved in 100 parts of 23 per cent. oleum. 10 parts of acetic anhydride are then added, and the solution stirred at 30° to 40° until a test portion diluted with water no longer gives a red but instead a yellow precipitate. The solution is then poured into ice and water with good stirring, so as to avoid local heating, and the precipitate filtered off and washed acid-free.

α-**Benzoylaminoanthraquinone,** which forms glistening, greenish-yellow, felted needles, m.p. 255° to 256°, is prepared by heating α-aminoanthraquinone with an equal weight of benzoyl chloride in ten times the weight of nitrobenzene at 180° to 190° until the evolution of hydrochloric acid ceases. On cooling, the benzoyl compound crystallises out, and is filtered off and washed free of nitrobenzene with alcohol.

1 : 4-**Diaminoanthraquinone—**
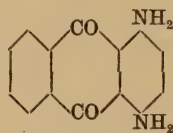
—violet needles, m.p. 268°. Very soluble in benzene and nitrobenzene, less so in alcohol, and sparingly in methyl alcohol. It is most conveniently crystallised from alcohol. It is more strongly basic than the monoaminoanthraquinones, and dissolves to an almost colourless solution in hydrochloric acid. Its solution in sulphuric acid is yellow, but on adding boric acid to this solution and warming the colour changes to crimson. The diacetyl derivative forms reddish-yellow needles, m.p. 271°.

The preparation of this compound from α-acetylaminoanthraquinone has been described by Römer (*Ber.*, **15**, 1790), and the method patented in G.P.'s 125391 and 135561 (Bayer). 10 kg. of α-acetylaminoanthraquinone are dissolved in 100 kg. of sulphuric acid (66° Bé), keeping the temperature during solution below 15° to prevent hydrolysis. 12·5 litres of mixed acid containing 20 per cent. of HNO_3 are then added slowly, the temperature being maintained at 15°. The nitration proceeds quickly, and is finished in about an hour. While the external cooling is continued, 60 kg. of ice is added, which causes separation of the nitro body in a crystalline form. This is filtered off and washed with cold water. It is then purified by crystallisation from ten times its weight of glacial acetic acid or pyridine. Pure 1-acetylamino-4-nitroanthraquinone forms golden yellow crystals insoluble in water, dilute acids, or alkalies, slightly soluble in alcohol, ether, and ligroin, and easily soluble in aniline. It crystallises particularly well from epichlorhydrin in long reddish-yellow needles, melting at 256° to 258°.

The purified nitro body is now hydrolysed by heating it with five times its weight of 80 per cent. sulphuric acid at 90° to 100° for half to one hour. Or the nitration solution may be heated directly, without isolating the acetylaminonitroanthraquinone, though this, of course, gives a less pure aminonitro compound. After cooling, the solution is run into water and the precipitate filtered off and washed acid-free. 1-Amino-4-nitro-anthraquinone is a red powder, insoluble in water and sparingly soluble in alcohol. It may be crystallised from epichlorhydrin as beautiful red needles, melting at 290° to 295°.

The reduction of the aminonitro compound is carried out by stirring 10 kg. of the finely powdered substance into 400 litres of water, adding a solution of 20 kg. of 70 per cent. sodium sulphide in 20 kg. of 23 per cent. caustic soda and warming at water-bath temperature. A green solution of the hydroxylamine derivative is formed at first, but this soon changes to the diamine, which separates as a brown crystalline precipitate. When reduction is complete, the diamine is filtered off, washed with water, and purified by dissolving it in dilute hydrochloric acid and reprecipitating. It may be crystallised from aniline as large dark violet bronzy crystals, which contain aniline of crystallisation.

The amino group of the α-aminoanthraquinone may alternatively be protected during nitration by acylation with oxalic acid, as described by Noelting and Wortmann (*Ber.*, **39**, 643). This is a method which has not been much used in the preparation of dyestuff intermediates, or, indeed, in any department of synthetic chemistry, but is certainly worthy of consideration as a technical method.

Noelting and Wortmann prepared the oxamic acid of α-aminoanthraquinone, $C_{14}H_7O_2.NH.CO.COOH$, by heating the amino compound with five times its weight

of crystalline oxalic acid for two days at 150° to 160°. The melt was then boiled out with water, filtered, washed with alcohol and ether, and dried for half an hour at 120°. The melting-point of the oxamic acid is 226°. It was nitrated by suspending it in concentrated sulphuric acid and adding mixed acid (containing 25 per cent. of HNO₃) at 5°. The nitro body separated as a yellow precipitate, which was filtered off through asbestos. It was hydrolysed by soda to the aminonitro compound, which, after crystallisation from nitrobenzene, melted at 296°, and was, therefore, purer than that obtained by Römer (m.p. 290° to 295°). The reduction was carried out as before by sodium sulphide.

1 : 4-Diaminoanthraquinone is used in the preparation of Algol Red 5G (which is simply the dibenzoyl derivative) and of Helindone Brown AN.

Halogen Derivatives of α-Aminoanthraquinone.

The chlorination of the free base with chlorine apparently, to judge by the literature, yields mixtures of various chloro derivatives, including N-chloro as well as nuclear substituted compounds, from which nothing definite can be isolated. It is otherwise with the bromination of α-aminoanthraquinone, which yields, according to the conditions employed, either the 2-bromo or the 2 : 4-dibromo derivative in fairly satisfactory yield. However, the 4-chloro derivative may also be obtained, as shown in G.P. 199758, if the amino group is first acylated.

1-**Amino**-2-**bromoanthraquinone**—
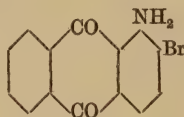
—orange crystals from glacial acetic acid, m.p. 180° to 181°. Its solution in **concentrated** sulphuric acid is yellow, and in 40 per cent. oleum bluish-violet.

The preparation of this substance is described in G.P. 160169. 20 parts of α-aminoanthraquinone is obtained in a finely divided condition by solution in sulphuric acid and reprecipitation with water. It is then stirred into 500 parts of glacial acetic acid and slowly heated to the boil, while a solution of 15 parts of bromine in 100 parts of glacial acetic acid is gradually added. When bromination is complete, the solution is cooled, and the bromamino compound filtered off. It is recrystallised from glacial acetic acid.

1-Amino-2-bromoanthraquinone can be methylated as follows (G.P. 288825) to produce 1-**methylamino**-2-**bromoanthraquinone** :
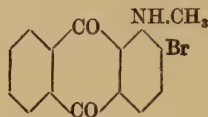
1 part of 1-amino-2-bromoanthraquinone, 4 parts of 96 per cent. sulphuric acid, and 4 parts of dimethyl sulphate are heated at 185°, until a test portion dissolved in

40 per cent. oleum no longer gives the violet solution of the aminobromo compound, but instead a brownish-yellow. The solution is then cooled, 12 parts of water are stirred in with external cooling, and the precipitated sulphate filtered off and washed acid-free.

1-Methylamino-2-bromoanthraquinone forms red crystals, m.p. 170° to 172°.

1-Amino-2 : 4-**dibromoanthraquinone :**
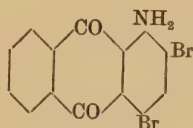
Fiery red felted needles, m.p. 226°, sparingly soluble in alcohol, ether, benzene, and glacial acetic acid, but easily soluble in hot nitrobenzene and pyridine.

A method of preparing this derivative by the action of bromine vapour on dry α-aminoanthraquinone spread in thin layers in a closed vessel, is described in G.P. 115048. But, according to Ullmann and Eiser (*Ber.*, 1916, **49**, 2165), the method is unsatisfactory. They prepare the substance as follows : 44·6 gms. of α-amino-anthraquinone are dissolved in 75 c.c. of nitrobenzene by heating to 150° to 160° in a flask fitted with a reflux condenser. A mixture of 75 gms. of bromine and 25 c.c. of nitrobenzene is slowly dropped in, with frequent shaking. The solution is then heated for three hours more at 160°, after which it is allowed to cool. The dibromo compound which crystallises out is filtered off and washed with alcohol. The yield is 61 gms. or 80 per cent., the product so obtained melting at 222°. By steam-distilling the nitro-benzene from the mother liquor, 12 gms. of a less pure product, melting at 199°, is recovered.

The bromine atom in the 4-position in this substance readily reacts with aromatic amines to produce mono-substituted 1 : 4-diamines, which are blue in colour, and which, on sulphonation, yield blue acid colours for wool. Alizarine Sky Blue is an example.

This 4-bromo atom is also labile in other ways. For instance, it is replaced by hydroxyl on heating the substance with sulphuric acid, thus producing 1-**amino**-2-**bromo**-4-**hydroxyanthraquinone :**
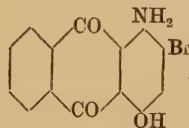
According to G.P. 203083 (E.P. 28104, 1907), 10 parts of 1-amino-2 : 4-dibromoanthra-quinone are warmed to 100° to 110° with 100 parts of monohydrate till a test portion dissolved in pyridine no longer gives a bluish-red solution. The melt is then poured into water, the precipitate filtered off, washed till neutral, and dried. It melts at 243° with decomposition, and gives a yellow solution in sulphuric acid, or if boric acid is added, a bluish-red solution.

It is used in the preparation of a dihydroxy-indanthrene, Algol Blue 3G.

1-**Amino**-4-**chloroanthraquinone**—
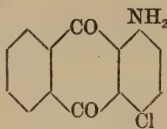
—red needles, m.p. 179° to 180°. Moderately soluble in hot xylene, amyl alcohol, and glacial acetic acid; soluble in nitrobenzene.

As mentioned above, this substance cannot be prepared by direct chlorination of α-aminoanthraquinone, but if the amino group is first acylated, chlorination of the acyl derivatives in suspension or solution in various solvents, such as water, acetic acid, carbon tetrachloride, etc., yields the 4-chloro derivative (G.P. 199758).

10 parts of 1-acetylaminoanthraquinone are stirred with 80 to 100 parts of glacial acetic acid. 10 parts of crystalline sodium acetate are added, and the whole heated at 80° on the water-bath, while chlorine is passed through in excess. The solution is cooled, filtered, and the product washed with water and dried. 1-Acetylamino-4-chloroanthraquinone is thus obtained as yellow crystals, which, after recrystallisation from glacial acetic acid, melt at 203° to 204°.

The acetyl compound is easily hydrolysed by heating with 80 per cent. sulphuric acid for an hour at 90° to 100°, and thus yields 1-amino-4-chloroanthraquinone.

1-**Methylaminoanthraquinone**—
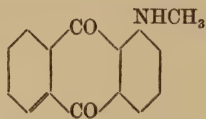
—yellowish-red needles, m.p. 167°.

This is prepared like α-aminoanthraquinone by amidation of the α-sulphonic acid, using, instead of ammonia, methylamine, as described in G.P. 175024 (Bayer). But, as in the case of the amino compound, improved yields are obtained if provision is made for dealing with the sulphite produced in the reaction. In G.P. 256515 (Badische), an oxidising agent, potassium bromate, is added :

100 parts of potassium anthraquinone-α-sulphonate, 600 parts of 6 per cent. aqueous methylamine solution, and 13 parts of potassium bromate, are heated and stirred in an autoclave at 150° for five or six hours. The methylaminoanthraquinone separates in a pure crystalline condition, and merely requires filtering off and washing with water.

The bromination of 1-methylaminoanthraquinone under special conditions, as described in G.P. 164791, leads to 1-methylamino-4-bromoanthraquinone :
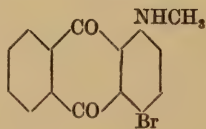
10 parts of 1-methylaminoanthraquinone are dissolved in 100 parts of warm pyridine, and the solution heated on the water-bath, while 6 to 8 parts of bromine are

gradually added. Heating is continued for one to two hours. On cooling, reddish-brown needles of the bromo compound separate and are filtered off and washed free of pyridine. The substance melts at 194°. Its solution in warm 40 per cent. oleum is deep blue.

α-**Chloroanthraquinone**—
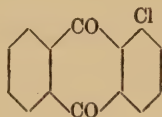
—yellow needles, m.p. 162°. Easily soluble in hot benzene, glacial acetic acid, and amyl alcohol. Crystallises well from alcohol. Its solution in sulphuric acid is yellowish-brown.

α-Chloroanthraquinone is prepared from anthraquinone-α-sulphonic acid by replacement of the sulpho group by chlorine. Several methods of carrying out this replacement have been used, including the use of chlorine gas (G.P. 205195) and thionyl chloride (G.P. 267544), but the best method is that involving the use of nascent chlorine developed from sodium chlorate and hydrochloric acid, as already described in the case of β-chloroanthraquinone. The application of this method to the preparation of α-chloroanthraquinone is thus described by Ullmann and Ochsner (*Ann.*, **388**, 2):

In a 3-litre flask fitted with a reflux condenser and a rapid stirrer, 40 gms. of potassium anthraquinone-α-sulphonate, 170 c.c. of concentrated hydrochloric acid and 1,200 c.c. of water are heated to boiling, and into the boiling liquid a solution of 40 gms. of sodium chlorate in 200 c.c. of water is dropped through the condenser during three hours. The α-chloroanthraquinone separates immediately as a yellow precipitate, and no chlorine escapes. To complete the reaction the solution is boiled for an hour after the chlorate has all been added. The chloro compound is then filtered off, washed with hot water, and dried. The yield is 28·4 gms. or 95 per cent. of pure α-chloroanthraquinone.

An earlier method of preparation (G.P. 131538, Bayer) from α-aminoanthraquinone by diazotisation and application of the Sandmeyer reaction does not give good results.

α-Chloroanthraquinone is used for condensations with aminoanthraquinones to produce dianthrimides and trianthrimides.

α-Chloroanthraquinone may be converted into α-**aminoanthraquinone** by condensation with p-toluenesulphonamide, followed by hydrolysis of the toluene-sulphoylaminoanthraquinone :

$$C_{14}H_7O_2.Cl \ + \ H_2N.SO_2.C_6H_4.CH_3 \ \longrightarrow \ C_{14}H_7O_2.NH.SO_2.C_6H_4.CH_3$$

$$\longrightarrow \ C_{14}H_7O_2.NH_2 \ + \ SO_3H.C_6H_4.CH_3$$
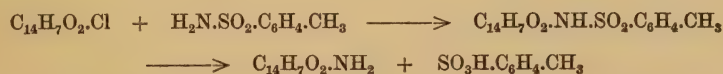
The process is thus described by Ullmann and Fodor (*Ann.*, **380**, 319):

5 gms. of α-chloroanthraquinone, 5 gms. of p-toluenesulphonamide, 4 gms. of potassium carbonate, 0·2 gm. of copper acetate, and 0·1 gm. of copper powder are stirred with 50 c.c. of nitrobenzene and heated at 180° to 200° for three hours. The

solution is finally brownish-yellow in colour. The nitrobenzene is now distilled off with steam, and the residual aqueous suspension filtered. The solid obtained melts at 218°. It is recrystallised from glacial acetic acid, and thus yields 6·5 gms. of α-toluene-sulphonylaminoanthraquinone as yellow needles, m.p. 228·5°. It is only slightly soluble in alcohol, moderately (1 in 25) in boiling glacial acetic acid and in toluene and xylene, and very soluble in pyridine and nitrobenzene.

The hydrolysis is carried out by dissolving the substance in ten times its weight of concentrated sulphuric acid. An orange-coloured solution is formed, but on slightly warming this changes to yellow, due to hydrolysis. The α-aminoanthraquinone is precipitated by pouring the solution into ice water, and is obtained quite pure (m.p. 243°). The overall yield is about 83 per cent.

This process has the great advantage over the usual one that it avoids the use of an autoclave, but it is undoubtedly more expensive.

α-**Hydroxyanthraquinone** (Erithroxyanthraquinone)—
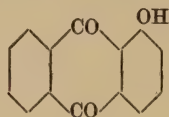
—orange needles, m.p. 193°. In powder form bright yellow. Sublimes easily. Slightly volatile in steam. Soluble in caustic soda solution, but not in ammonia or carbonate. Moderately soluble in alcohol, more so in benzene and ether.

This substance cannot be prepared by the usual alkali fusion of the corresponding α-sulphonic acid, since under the ordinary conditions of fusion the anthraquinone nucleus in this case is ruptured, and varying proportions of m-hydroxybenzoic and sulphobenzoic acids are formed. The replacement of the sulpho group by hydroxyl in the anthraquinone series, in fact, requires much less drastic conditions than those employed in the benzene or naphthalene series. In the present case, heating at moderate temperatures with very dilute caustic soda or milk of lime (G.P. 172642) or carbonates (G.P. 197649) will effect the replacement.

25 kg. of potassium anthraquinone-α-sulphonate are heated with 18 kg. of lime and 400 litres of water in a stirring autoclave for three to four hours at 190°. After cooling to about 100°, the reaction mixture is acidified with hydrochloric acid, when the α-hydroxyanthraquinone separates as a yellow precipitate in very pure condition. The yield is said to be quantitative (G.P. 172642).

A method of preparation from α-aminoanthraquinone through the diazo compound is described in G.P. 97688, but this does not work well, and is unnecessarily circuitous.

α-**Methoxyanthraquinone :**
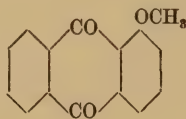
The preparation of this substance directly from the α-sulphonic acid by boiling with methyl alcohol and caustic soda is described in G.P. 156762 (Bayer), but the

yield obtained is too small to make the method practicable. It can be prepared, however, by methylation of α-hydroxyanthraquinone under the special conditions given in G.P. 243649 (Meister Lucius and Brüning).

100 gms. of the dry sodium salt of α-hydroxyanthraquinone are stirred into 200 gms. of the methyl ester of *p*-toluenesulphonic acid heated at 180°. The melt soon thickens, due to the separation of the methoxy compound as a pale yellow substance. After cooling, the mass is rubbed up with alcohol, filtered, the residue washed with water, and then with a little alcohol, and dried. The yield is said to be nearly theoretical.

α-Hydroxy- and α-methoxyanthraquinone, when nitrated, yield in each case chiefly the 4-nitro derivative. The nitro compounds, on reduction with sodium sulphide, give the corresponding amino compounds, whose benzoyl derivatives constitute the dyestuffs Algol Pink R (1-benzoylamino-4-hydroxyanthraquinone) and Algol Scarlet G (1-benzoylamino-4-methoxyanthraquinone).

Quinizarin :
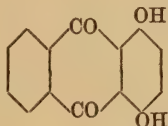
(For properties and another method of preparation, see p. 208.)

The preparation of quinizarin from anthraquinone or 1-hydroxyanthraquinone has been described in a series of patents by Bayer and Co. (G.P. 81960, 81245, 161954, 162792). The methods used, which are due to R. E. Schmidt, consist in subjecting the anthraquinone or its derivative to the oxidising action of sulphuric acid, assisted by sodium nitrite or mercuric sulphate, in presence of boric acid. It seems, however, to be difficult to obtain unitary products by these methods.

Quinizarin can also be prepared from 1-hydroxyanthraquinone by chlorination to the 4-chloro derivative, and replacement of the chlorine atom by hydroxyl through heating with sulphuric acid and boric acid at a high temperature (Ullmann and Conzetti, *Ber.*, 1920, **53,** 826). Ullmann and Conzetti used sulphuryl chloride for the chlorination of 1-hydroxyanthraquinone, but chlorine gas can also be used, as described in E.P. 209694 (Thomas and Scottish Dyes).

A solution of 120 lbs. of 1-hydroxyanthraquinone in 640 lbs. of 98 per cent. sulphuric acid is circulated at 70° to 75° through a tower up which chlorine is passing at the rate of 5 to 6 lbs. per hour. After 80 lbs. of chlorine have been passed, a sample of the solution is taken and the crude 1-hydroxy-4-chloroanthraquinone precipitated by pouring into water, filtered, and washed acid-free. The chlorine content is determined. If this is about 13·7 per cent. and the melting-point is 180° to 181°, the chlorination is complete.

Without isolating the 4-chloro body, 80 lbs. of boric acid is added to the solution, which is then heated for twelve hours at 160°, or for eight hours at 180°. The cooled solution is then run into water and the precipitated quinizarin isolated in the usual way. The yield obtained is slightly over 120 parts.

α-**Anthrol**—

—yellow plates, m.p. 152°, almost insoluble in water, but soluble in most organic solvents, the solutions showing a blue fluorescence.

This derivative of anthracene is prepared by fusion of the corresponding sulphonic acid with alkali. Reference has been made to the difficulty of preparing directly from anthracene in pure condition the anthracenemonosulphonic acids (p. 214). The α-sulphonic acid of anthracene is, therefore, usually prepared by reduction of anthraquinone-α-sulphonic acid or its salts. The method is described by R. E. Schmidt (*Ber.*, 1904, **37,** 70).

30 gms. of potassium anthraquinone-α-sulphonate is warmed with 500 to 750 c.c. of 20 per cent. ammonia and 70 gms. of zinc dust for ten to twelve hours on the water-bath. The solution, at first intensely reddish-yellow, slowly decolourises. When the reduction is finished, the solution is filtered hot, and, on cooling, potassium anthracene-α-sulphonate crystallises in colourless leaflets.

The sulphonate is then fused at 270° to 280° (the paper referred to gives 170° to 180° as the fusion temperature, but this is probably a misprint) with 5 parts of caustic potash. The finished melt is dissolved as quickly as possible in water, the solution acidified with hydrochloric acid and the α-anthrol, which separates as pale grey flocks, filtered off. It is purified by dissolving it in boiling glacial acetic acid, adding animal charcoal and boiling a short time to decolourise the solution. After filtering, water is added till a slight cloudiness appears, when, on cooling, the α-anthrol crystallises in pale yellow lustrous plates.

Sircar (*J.C.S.*, 1916, **109,** 774) carried out the fusion at 250° to 260° for twenty-five minutes, using 2 gms. of the α-sulphonate and 10 gms. of caustic potash. The cooled melt was then diluted with 4 to 5 c.c. of water, 6 to 7 c.c. of concentrated hydrochloric acid added, and the whole poured into 100 c.c. of water. On recrystallising the crude product from acetic acid a yield of 1 gm. of α-anthrol was obtained.

α-Anthrol is used in making vat dyes by condensing it with isatin derivatives. Apparently in such condensations it reacts in its ketonic form :
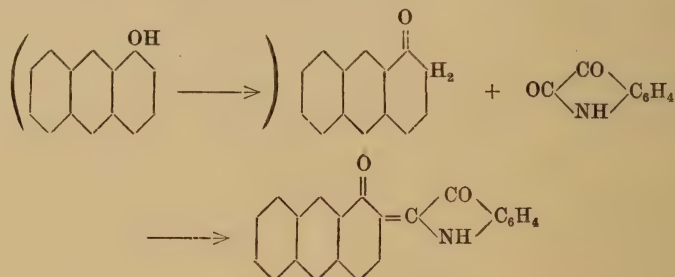
Using dibromoisatin, Alizarin Indigo is obtained.

Anthrarufin—
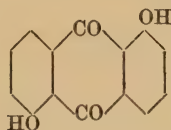
—crystallises in yellow needles or tablets, m.p. 280°, insoluble in water, sparingly soluble in alcohol, ether, or glacial acetic acid, but moderately soluble in benzene. Its solution in sulphuric acid is intense crimson in colour. In caustic alkalies it dissolves to a red solution.

This substance is obtained from anthraquinone-1 : 5-disulphonic acid by heating at high temperatures with milk of lime (E.P. 25541 of 1903; G.P. 170108, Bayer).

In an autoclave fitted with a stirrer, 20 parts of sodium anthraquinone-1 : 5-disulphonate, 30 parts of slaked lime, and 400 parts of water, are heated at 180° to 190° for twelve hours. The product is acidified with hydrochloric acid, and the precipitated anthrarufin filtered off.

According to a patent of Iljinskij and Wedekind and Co. (E.P. 25738 of 1903), if a **salt** (sodium or potassium) of the anthraquinonedisulphonic acid is used, as in the Bayer patent, the caustic alkali set free in the reaction, which proceeds mainly as in the equation—

$$C_{14}H_6O_2(SO_3Na)_2 + 2Ca(OH)_2 = C_{14}H_6O_2(OH)_2 + 2CaSO_3 + 2NaOH$$
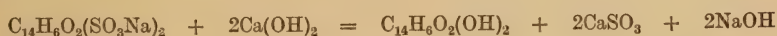
—causes the production of much dark smeary impurity, reduction taking place to some extent. They proposed, therefore, to use the calcium salt of the disulphonic acid, together with some calcium chloride, and recommended the following method : 100 parts of the calcium anthraquinone-1 : 5-disulphonate are stirred with 500 parts of hot water, in this are slaked 100 parts of lime, and 30 parts of sodium nitrate and 100 parts of 20 per cent. calcium chloride solution added. The whole is stirred under pressure in a digester at 180° to 220° until no trace of hydroxysulphonic acid can be detected. The product is then precipitated by addition of hydrochloric acid. The yield obtained is 50 parts of pure anthrarufin.

The conversion of the disulphonate to anthrarufin can also be carried out with aqueous sodium carbonate at 190° to 200° (G.P. 197649, Bayer).

Anthrarufin is used for the preparation of Alizarin Saphirol B and SE.

Diaminoanthrarufin—
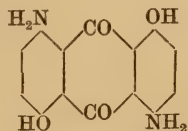
—dark violet needles, insoluble in water.

Diaminoanthrarufin can be prepared by dinitration of anthrarufin and reduction of the product, but it is difficult to obtain it pure in this way, since the nitro groups enter other positions besides the 4- and 8-, and a complex mixture of several nitro-anthrarufins is obtained.

It is more satisfactorily prepared by a method described in two patents of Bayer's, G.P. 158531 and 170728. Anthraquinone-1 : 5-disulphonic acid is converted into 1 : 5-diphenoxyanthraquinone by heating with phenol and caustic potash. On nitrating the diphenoxy compound, the nitro groups first enter the phenyl nuclei, and then enter the 4- and 8-positions only of the anthraquinone nucleus. The resulting compound is easily hydrolysed with dilute alkali to 4 : 8-dinitroanthrarufin, which may then be reduced to diaminoanthrarufin :
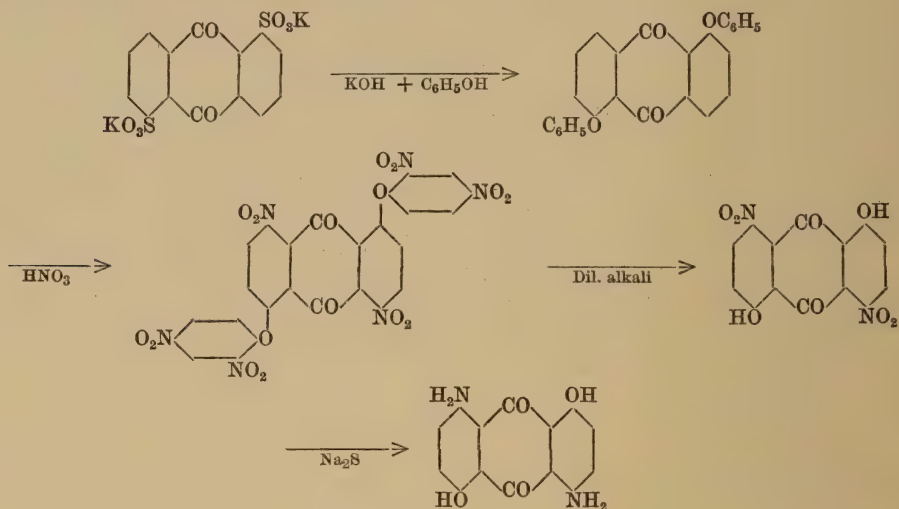
A mixture of 160 kg. of phenol and 50 kg. of caustic potash is heated to 140°, and 20 kg. of sodium anthraquinone-1 : 5-disulphonate added. The whole mass is then heated to 180°, and kept at this temperature until the sulphonate has nearly all disappeared. After cooling, the melt is stirred with hot water and filtered. The diphenoxy compound so obtained may be purified by crystallisation from glacial acetic acid or nitrobenzene, and is obtained as long yellow needles, m.p. 215°, which dissolve in most organic solvents to yellow solutions. Its solution in sulphuric acid is pure blue in colour, but on warming, changes to orange-red.

The nitration is carried out by dissolving 20 kg. of diphenoxyanthraquinone in 250 kg. of 100 per cent. sulphuric acid, and adding, at 0° to 5°, 40 to 50 litres of mixed acid containing about 50 per cent. of nitric acid. The solution is then stirred at the ordinary temperature until the hexanitro compound, which is very sparingly soluble in sulphuric acid, has completely separated. The mixture is poured into water, and the product filtered off, washed, and dried. It may be purified by crystallisation from nitrobenzene, and forms fine grey needles. It dissolves at 200° in boric-sulphuric acid to a blue-violet solution. It is hydrolysed, by warming with dilute alkali, to dinitroanthrarufin and 2 : 4-dinitrophenol. The former is then reduced in the usual way with sodium sulphide to diaminoanthrarufin.

Diaminoanthrarufin, on acylation of the amino groups with benzoyl chloride, anisoyl chloride, etc., yields blue or violet vat dyes of great fastness.

Nitration of Anthraquinone.

The direct nitration of anthraquinone by the ordinary method produces chiefly α-derivatives—that is, 1-nitro- and 1:5- and 1:8-dinitroanthraquinones. As in sulphonation, nitration of anthraquinone cannot be carried out so as to form the mononitro compound without at the same time forming a large proportion of dinitro compounds, and the general experience of workers on these substances has been that they are difficult to prepare in a reasonable state of purity. This, no doubt, accounts for the fact that most anthraquinone derivatives are obtained through the sulphonic acids. Ullmann, however, claims good results for the following preparation of α-nitro-anthraquinone (Ullmann and van der Schalk, *Ann.*, **388**, 203), based on a method given by Lauth (*C. r.*, 1903, **137**, 662):

20·8 gms. of anthraquinone are dissolved in 125 c.c of concentrated sulphuric acid, and the solution is warmed to 50°. At this temperature 7·6 c.c. of nitric acid (D 1·4— *i.e.*, 65 per cent.) are slowly added, the temperature being maintained about 50°. This quantity of nitric acid is about 10 per cent. in excess of the theoretical requirement for mononitroanthraquinone. When the nitric acid is all added, the mixture is cooled and poured on ice. The precipitate is filtered off, and washed acid-free with hot water. The yield of this product is 25 gms., and its melting-point 217°. But it contains besides α-nitroanthraquinone some unchanged anthraquinone and dinitro-anthraquinones. This crude product is extracted with toluene, which leaves 2 gms. of dinitro compounds undissolved, and on evaporation of the toluene solution to crystallising point the α-nitroanthraquinone is obtained, though even then it is contaminated with anthraquinone and with 1:8-dinitroanthraquinone, etc.

Another method of purification of the crude product is given in G.P. 281490 (Ullmann). This depends on distillation in a vacuum under 7 mm., when the α-nitro compound distils undecomposed at 270° to 271° as a pale yellow liquid.

For the preparation of α-**aminoanthraquinone,** however, according to Ullmann and van der Schalk (*loc. cit.*), the moist crude nitro product as obtained above may be used direct. It is rubbed with 40 gms. of crystalline sodium sulphide ($Na_2S.9H_2O$) and the dark thick paste gradually diluted, while being stirred, with 700 c.c. of boiling water. The mixture is then heated until a test portion, on filtering off the solid and rubbing it up with a little sodium sulphide, no longer becomes green. About twenty minutes is required to reach this point. The suspended α-aminoanthraquinone is then filtered off and boiled up twice with water. The yield is 21·9 gms. (from 20·8 gms. of anthraquinone) or 98 per cent. The melting-point of the product is given as 243°, which is the melting-point of the pure substance as obtained by Ullmann. This is probably not the case, however, the figure 243° being more probably the melting-point of the several times recrystallised product.

When anthraquinone is nitrated with more than two molecular equivalents of concentrated nitric acid, a mixture of **dinitroanthraquinones** is formed. Römer (*Ber.*, **16**, 366) gives the following particulars: A solution of 10 gms. of anthraquinone in concentrated sulphuric acid is treated with 10 gms. of nitric acid (D 1·48, or 86 per cent.). The mixture is allowed to stand for several days, and is then poured into

water and the precipitate filtered off, washed acid-free, and dried. A mixture of dinitroanthraquinones obtained in some such way as this was found by Battegay and Claudin (*Bull. Soc. Ind. Mulhouse*, 1920, **86**, 628-631) to contain 37 per cent. of 1 : 5-, 37 per cent. of 1 : 8-, 4·2 per cent. of 1 : 7-, 3·6 per cent. of 1 : 6-, 6 per cent. of 2 : 6-, and 4 per cent. of 2 : 7-dinitroanthraquinones.

The mixture of dinitro compounds is used in the preparation of the Anthracene Blues. But 1 : 5-dinitroanthraquinone, owing to its exceptional properties, may be separated fairly readily from the mixture by extracting the other dinitro compounds with alcohol or acetone in which the 1 : 5-dinitro compound is insoluble. The extraction is continued until a test portion of the residue dissolves in potassium stannite solution with a pure blue colour. The residue is then recrystallised from nitrobenzene, and 1 : 5-dinitroanthraquinone thus obtained as large yellow prisms, m.p. 422°.

Noelting and Wortmann (*Ber.*, **39**, 643) have shown that 1 : 5- and 1 : 8-**diaminoanthraquinones** may be obtained from the crude mixture of dinitro compounds as prepared by Römer by reducing the whole mixture, and then separating the diamino compounds by differences in basicity.

250 gms. of the dinitroanthraquinone mixture, as obtained by Römer's method, is stirred into an aqueous solution of sodium sulphide. The mixture dissolves to a green solution, and this is gently boiled for an hour, during which the red diamines separate. The precipitate is filtered off, washed, and dried. The yield is almost quantitative, about 200 gms. This mixture is then rubbed with 400 c.c. of water and 800 c.c. of concentrated sulphuric acid added, which effects complete solution of the diamines. The solution is diluted with 400 c.c. of water, heated to boiling, and filtered, if necessary, through glass wool. After standing for twenty-four hours, a considerable precipitate has separated, and this is filtered off. It consists of the sulphate of 1 : 5-diaminoanthraquinone, and this is dissociated by stirring with a large volume of water, the diamine being filtered off, washed, and dried. The yield is 78 gms. It may be purified by crystallisation as sulphate from a mixture of equal volumes of water and sulphuric acid, the sulphate being afterwards dissociated. It is thus obtained in pure condition, m.p. 319°.

The sulphuric acid filtrate from the 1 : 5-diaminoanthraquinone sulphate is poured into several litres of cold water. The precipitated bases are filtered off, boiled up with water, again filtered, washed, and dried. The dry product weighs about 120 gms. It is boiled up with two and a half times its weight of acetic anhydride, and an equal weight of glacial acetic acid for an hour under reflux. After standing for twenty-four hours, the separated diacetyl compound is filtered off, washed, and dried. It is then hydrolysed by heating for half an hour with ten times its weight of sulphuric acid at 80°. The solution is poured into water and partly neutralised by ammonia to set free the base, which is then filtered off. It may be crystallised from alcohol, glacial acetic acid, nitrobenzene, or pyridine. In this way, a yield of 70 gms. of 1 : 8-diaminoanthraquinone, m.p. 262°, is obtained.

1 : 5-**Dichloroanthraquinone**—
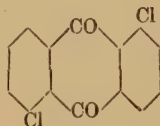
—pale yellow crystals, m.p. 251°. Insoluble in water, soluble in organic solvents. Best crystallised from glacial acetic acid.

It is prepared from anthraquinone-1 : 5-disulphonic acid by the action of sodium chlorate and hydrochloric acid, as described in G.P. 205195.

20 parts of sodium anthraquinone-1 : 5-disulphonate are dissolved in a mixture of 400 parts of water and 40 parts of hydrochloric acid (20° Bé). The solution is heated to boiling, and a solution of 40 parts of sodium chlorate in 300 parts of water slowly added until no further precipitate of the dichloro compound is formed. This usually requires several hours' boiling. The dichloro compound is then filtered off, washed with water, and purified if necessary by recrystallisation from glacial acetic acid.

1 : 5-Dichloroanthraquinone is used in making Indanthrene Violet RN.

Benzanthrone—

—crystallises in fine pale yellow needles, m.p. 170°, soluble in alcohol and other organic solvents. It dissolves in sulphuric acid to an orange-red solution with an olive-green fluorescence.

Benzanthrone is prepared by heating anthranol, an acid reduction product of anthraquinone, with glycerol and sulphuric acid, the reaction being analogous with the formation of quinoline from aniline :
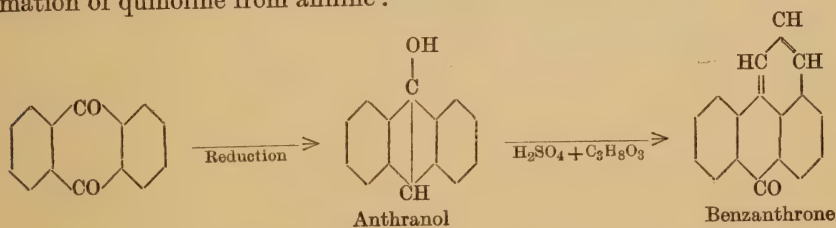
(a) **Anthranol.**—This is best prepared, as in G.P. 201542 (Bayer), by dissolving 10 parts of anthraquinone in 150 parts of concentrated sulphuric acid and gradually adding to the well-stirred solution 2·5 parts of aluminium powder, the temperature being kept at 30° to 40°. Much frothing takes place. When the reaction is over, the anthranol may be precipitated by running the solution into water, and is filtered off. Recrystallised from glacial acetic acid, it forms lustrous pale yellow needles, m.p. 163° to 170°. The melting-point, even of the pure substance, is indefinite because, on fusion, anthranol changes partly into its tautomeride, anthrone (m.p. 154°) :
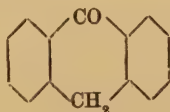
(*b*) **Benzanthrone.**—To a solution or suspension of 10 parts of anthranol in 150 parts of sulphuric acid (62° Bé=82 per cent.), 10 parts of glycerol are added. The mixture is cautiously heated. At about 120°, a vigorous reaction sets in, the solution becomes red and sulphur dioxide is evolved. After four hours' further heating at 120°, the cooled solution is poured into water and the benzanthrone separates as olive-green flocks, which are filtered off, washed, and boiled for half an hour with thirteen times the weight of 1 per cent. caustic soda solution, then filtered and dried. It may be purified by crystallisation from alcohol (G.P. 176018, Badische).

Benzanthrone forms the starting-point of a series of very fast blue, violet, and green vat dyes, of which the first, Indanthrene Dark Blue BO, is obtained by fusing benzanthrone with caustic potash.

STABILISED DIAZO COMPOUNDS

A LARGE number of insoluble azo colours—the so-called " ice colours "—are produced on the fibre (cotton) by padding the material with a solution of sodium β-naphtholate, or other suitable phenolic compound, drying off and then passing the padded material through a solution of a diazotised amine, when coupling takes place and the colour is formed on the fibre. This method of dyeing was initiated by the firm of Read, Holliday, and Sons in 1880, and has been greatly extended within the last ten years by the introduction of β-oxynaphthoic anilide (Naphthol AS), and similar substances by the Griesheim-Elektron firm as variants on β-naphthol, which was formerly the only substance used as second component in such colours.

As is well known, the diazo compounds of aromatic amines are very unstable substances, and are generally formed in an ice-cold acid solution of the amine by addition of sodium nitrite solution. In the dry state the pure diazo compounds are extremely explosive. The troublesome nature of the diazotisation process, and the difficulty of keeping the temperature low enough to avoid decomposition, led to efforts to obtain diazo compounds in a form which would be sufficiently stable to be capable of being stored, transported, and used by the dyer as required by simple solution in water. This problem was successfully solved in several different ways chiefly by the Badische Anilin- und Soda-Fabrik, Meister Lucius and Brüning, and Cassella and Co. These firms, and others using their processes, now market a large range of stabilised diazo compounds.

(a) Nitrosamines or Isodiazotates.

The first, and probably the most successful, solution of the problem was discovered by Schraube and Schmidt, and patented by the Badische Anilin- und Soda-Fabrik in G.P. 78874, and a series of additional patents. It consists in the transformation of the ordinary diazonium salt by the action of alkali into a tautomeric form, which is stable at moderate temperatures even when dry. The diazonium salt produced in the ordinary diazotisation is considered to have the constitution :

$$R\text{—}N\text{—}Cl$$
$$\overset{\|}{N}$$
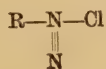
When its solution is poured into excess of warm alkali, the diazonium salt is transformed into a substance whose constitution is still a matter of controversy. Schraube and Schmidt attributed to it the structure of a metallic derivative of a nitrosamine (I), while others consider it a salt of the *anti*-form of an **isodiazotic acid** (II), of which two stereoisomeric forms are theoretically possible :

(I) $R\text{—}N\text{—}Cl + 2NaOH \longrightarrow R.N(Na).NO + NaCl + H_2O$
      $\overset{\|}{N}$

(II) $R\text{—}N\text{—}Cl + 2NaOH \longrightarrow R\text{—}N + NaCl + H_2O$
       $\overset{\|}{N} \qquad\qquad\qquad N.ONa$
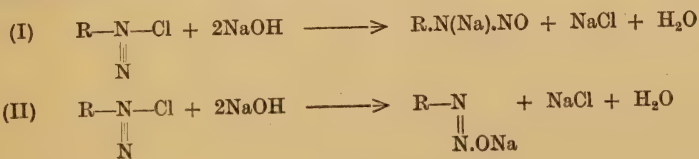
The evidence for either formula cannot be entered into here. The important practical points are (1) that substances of this nature are stable, (2) that they do not couple with phenols in alkaline solution, (3) that they are sparingly soluble in concentrated alkali or in common salt solution, and are, therefore, readily isolated, (4) that they can be transformed back into diazonium salts simply by dissolving them in water and acidifying the solution.

The method of preparation of these nitrosamines or isodiazotates is indicated by the following example from G.P. 78874 :

The diazonium chloride, prepared from 138 parts of *p*-nitroaniline in the usual way in a solution of about 10 per cent. concentration, is run into 8,000 parts of hot 18 per cent. caustic soda solution with good stirring. Stirring is continued until a sample of the solution no longer produces a colour on adding it to an alkaline solution of *β*-naphthol. This stage is reached in a very short time. On cooling, the product separates in yellow needles, which are filtered off and pressed.

The amines which most readily undergo this transformation are those containing negative substituent groups, such as the nitro-, chloro-, or nitrochloro-amines. These can be transformed at 10° to 15°, using caustic soda, or at 40° to 50°, using sodium carbonate as alkali. Thus, the preparation of the stable diazo compound of 2 : 5-dichloroaniline is thus described in G.P. 81134 :

168 parts of 2 : 5-dichloroaniline are dissolved in 350 parts of concentrated hydrochloric acid and 800 parts of water by heating. On cooling, the solution sets to a thick paste of crystals of the hydrochloride. To this, 300 parts of ice are added, the mixture is stirred, and a solution of 75 parts of sodium nitrite in 150 parts of water slowly run in. The 10 per cent. solution of diazonium salt so obtained is filtered from a little insoluble matter and quickly stirred into a solution of 2,400 parts of soda ash in 10,000 parts of water at 45°. After conversion to the nitrosamine is shown to be complete by the *β*-naphthol test, the yellow solution is filtered and solid caustic soda added until a cooled sample shows crystallisation. The whole is then allowed to stand until the separation is complete and the product filtered off.

Amines, such as the toluidines, *p*-anisidine, *α*-naphthylamine, benzidine, etc., which contain no negative substituents require a much higher temperature for the transformation which, in their case, proceeds best at 110° to 120° (G.P. 81202).

(b) Stabilisation by the Addition of Inorganic Salts.

It is shown in G.P. 85387 (Meister Lucius and Brüning) that solutions of diazonium salts can be made much more stable by addition of large excess of mineral acid. This increased stability enabled the solutions to be evaporated under reduced pressure at 45°. The explosive nature of the dry compounds is overcome by mixing the partially evaporated solution with an anhydrous inorganic salt, such as sodium sulphate, calcined alum, etc., which takes up the remaining water to form the hydrated salt, and thus gives a dry powder, said to be quite stable.

Thus, for example, in the case of *p*-nitroaniline, the stable diazonium salt is prepared by diazotising 14 kg. of *p*-nitraniline with 7 kg. of sodium nitrite and 17 kg. of

sulphuric acid (66° Bé) in the usual way at the highest possible concentration. The filtered solution of the diazonium sulphate is then evaporated in a lead- or copper-lined vacuum pan at 45° until it reaches a syrupy consistency. On mixing this with an equal weight of anhydrous sodium sulphate or calcined alum a dry powder is obtained. This comes on the market as Azophor Red PN. A stabilised tetrazo compound similarly prepared from dianisidine is sold as Azophor Blue D.

These products merely require to be dissolved in water to be ready for use.

In certain cases, particularly aminoazobenzene and other aminoazo compounds, addition of zinc chloride solution to the solution of diazonium chloride results in the formation of sparingly soluble double chlorides, which are stable (G.P. 89437, Meister Lucius and Brüning).

Cassella and Co. (G.P. 97933) found that a mixture of the diazonium sulphate with sodium bisulphate was remarkably stable. It is prepared as follows :

Into 80 kg. of concentrated sulphuric acid, a stream of nitrous fumes is led until 10 kg. has been absorbed. The solution of nitrosylsulphuric acid so formed is cooled and 30 kg. of *p*-nitroaniline added gradually. A clear and colourless solution of diazotised *p*-nitroaniline is formed. To this is added 120 kg. of anhydrous sodium sulphate. After a short time the mass sets solid. It is ground to a powder, which is not sensitive either to mechanical shock or to heat. It is sold under the name Nitrazol C.

Other stable diazo and tetrazo compounds are made in similar fashion.

A later patent of the same firm, G.P. 281098, states that the stability of the product is increased by partly neutralising the sulphuric acid with magnesia or magnesite before adding the sodium sulphate.

(c) Stable Diazonium Naphthalenesulphonates.

It was discovered by Becker (G.PP. 81039, 86367, etc.) that diazonium salts, on addition to solution of naphthalenesulphonic acids, form diazonium naphthalenesulphonates—*e.g.*, $NO_2.C_6H_4.N_2.SO_3.C_{10}H_7$. Those derived from naphthalene-α-sulphonic acid are sparingly soluble, and thus easily isolated. They are found to be quite stable if protected from sunlight and moisture. The naphthalene-β-sulphonates are too soluble to be isolated.

O. N. Witt, however, was able to prepare a double salt of *p*-nitrobenzenediazonium naphthalene-β-sulphonate with sodium naphthalene-β-sulphonate, which is sparingly soluble and separates as lemon yellow needles having the formula :

$$NO_2.C_6H_4.N_2.SO_3.C_{10}H_7 \ + \ NaSO_3.C_{10}H_7 \ + \ H_2O$$

This is prepared as follows (G.P. 264268):

A solution of 13·8 parts of *p*-nitroaniline in 100 parts of 50 per cent. sulphuric acid is cooled with ice and diazotised with 7 parts of sodium nitrite in concentrated solution. After filtering from traces of insoluble matter, a concentrated solution of 45 parts of free naphthalene-β-sulphonic acid ($C_{10}H_7.SO_3H+H_2O$) is added. The solution becomes orange-red in colour, and after a short time the double salt separates. The separation is completed at the lowest possible temperature, and the salt filtered, washed, pressed, and dried. It is sold as Paranil A.

CHAPTER XVI

MISCELLANEOUS INTERMEDIATES

I. Derivatives of the Cresols.

THE three cresols—
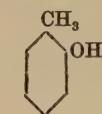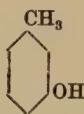
o-Cresol,   m-Cresol,   p-Cresol,
b.p. 191°   b.p. 202°   b.p. 203°

—are obtained chiefly from that fraction of the middle oil of coal tar which boils between 185° and 220°, the fraction which contains also most of the naphthalene. They are separated from the associated hydrocarbons and bases by extraction with caustic soda, and a crude mixture of the three isomers boiling between 185° and 205° is finally obtained, which constitutes the ordinary " cresylic acid." From this mixture pure o-cresol is obtained by fractional distillation, since its boiling-point is sufficiently distant from those of m- and p-cresols. The separation of m- and p-cresols is accomplished by chemical methods. The following methods of separation have been used:

(a) **Sulphonation Method.**—The mixture is sulphonated with rather less than its own weight of 94 per cent. sulphuric acid at about 100°. This produces a mixture of the monosulphonic acids—
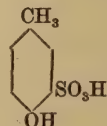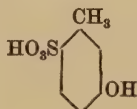
—from which p-cresolsulphonic acid can be separated by crystallisation fairly, but not quite, completely. The cresols are then recovered from their sulphonic acids by hydrolysis with superheated steam. p-Cresol is thus obtained in good purity, but the m-cresol contains a substantial proportion of p-compound.

(b) **Separation through the Calcium Salts.**—The mixture of m- and p-cresols is converted into calcium salts by treatment with lime. The calcium salts are then distilled with superheated steam, which decomposes the calcium salt of m-cresol only, so that m-cresol distils over, while the calcium salt of p-cresol remains unchanged, and is acidified to recover the p-cresol (G.P. 267210).

o-Cresol and p-cresol are used to a small extent as end components in azo dyes.

o-**Cresotinic acid** (o-Cresotic acid)—
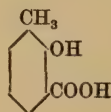
—crystallises in long flat needes, m.p. 163° to 164°, volatile in steam.

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This is prepared from *o*-cresol by the same method as that used in preparing salicylic acid from phenol. It is important to note that the sodium salt of *o*-cresol is spontaneously inflammable, so that the whole preparation must be carried through in one vessel. The product always contains some unchanged *o*-cresol (about 20 per cent.), and the cresotinic acid must, therefore, be purified by crystallisation from water.

Cresotinic acid is used, like salicylic acid, as an end component in azo dyes, especially in conjunction with diamines of the benzidine series. It is also used in the preparation of a few triphenylmethane dyes by condensation with benzaldehyde derivatives.

m-**Amino-***p*-**cresol methyl ether** (Cresidine)—

$$CH_3 \quad NH_2 \quad OCH_3$$
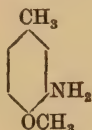
—crystallises in long rhombic prisms, m.p. 51·5°, b.p. 235°. It is almost insoluble in cold water, but sparingly soluble in hot water, and easily soluble in alcohol, ether, and benzene. Its hydrochloride is soluble in water.

Cresidine is prepared from *p*-cresol by the same series of operations as is used in making *o*-anisidine from phenol—*i.e.*, nitration, methylation, and reduction (Hofmann and Miller, *Ber.*, 1881, **14**, 573). Very little information is available with regard to the details of the process.

$$CH_3 \quad OH \longrightarrow CH_3 \quad NO_2 \quad OH \longrightarrow CH_3 \quad NO_2 \quad OCH_3 \longrightarrow CH_3 \quad NH_2 \quad OCH_3$$

Nitro-*p*-**cresol** forms yellow flat needles, m.p. 33·5°. According to Staedel (*Ann.*, **217**, 53), some dinitro-*p*-cresol is always formed along with the mononitro compound. The latter, however, can be separated by its volatility in steam.

Nitrocresol methyl ether forms pale yellow crystals, m.p. 8·5°, b.p. 274°. It is almost insoluble in alcohol.

Cresidine is used as a first and also as a middle component in azo dyes. In the former case it imparts to the colours derived from it, which are mostly reds containing naphtholsulphonic acids as end components, a brilliant bluish tone similar to that observed in dyes derived from *o*-anisidine.

II. Derivatives of Acenaphthene.

$$\overset{1}{H_2C}—\overset{2}{CH_2}$$
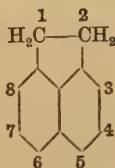
Acenaphthene crystallises in characteristic long needles, melting at 95° and boiling at 278°. It occurs in the last fractions of the heavy oil of coal tar, and in the fore-

runnings of the anthracene oil. Its separation is somewhat difficult, owing to the occurrence of a number of substances of similar properties in the same fractions. Fractional distillation and crystallisation are used to some extent, but these, applied in the ordinary way, do not yield a pure product. The fraction boiling between 275° and 285° gives a mass of crystals which, after separation from oil, contain about 50 per cent. of acenaphthene.

By a method described in G.P. 277110, pure acenaphthene may readily be separated from these mixed crystals. On mixing 50 kg. of the crystals with 50 kg. of the 240° to 260° fraction of coal tar (containing chiefly methyl naphthalenes), and distilling, the first fraction, up to 245°, remains liquid on cooling. The next fraction, 245° to 275°, about 30 kg. in weight, on cooling, deposits 6 kg. of fairly pure acenaphthene crystals. The third fraction, up to 285°, yields 11 kg. of an impure acenaphthene (60 to 70 per cent.), which can be purified by mixing it again with the 240° to 260° fraction and redistilling. A final purification can be given by recrystallising from alcohol.

Acenaphthenequinone—
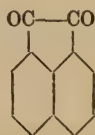
—crystallises and sublimes as yellow needles, m.p. 261°, very sparingly soluble in water. 100 gms. of glacial acetic acid at 15° dissolve 0·15 gm.

This, the only important derivative of acenaphthene, is prepared by oxidation of acenaphthene with chromic acid (Graebe and Gfeller, *Ann.*, 1893, **276**, 4). The yields obtained under the best conditions are not good, owing to the tendency for the oxidation to proceed further to form naphthalic acid. Another by-product formed is bisacenaphthylidene diketone :
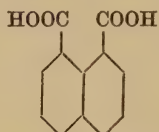
Naphthalic Acid
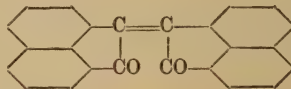
Bisacenaphthylidene Diketone

The preparation is described by Graebe and Gfeller as follows :

10 gms. of acenaphthene and 70 c.c. of glacial acetic acid are mixed in a basin of $\frac{3}{4}$ to 1 litre capacity and heated to 95° to 100°. The flame is then removed and 40 to 45 gms. of finely powdered commercial sodium dichromate (89 to 90 per cent.) added with good stirring. In a few moments a vigorous reaction sets in, the acetic acid boils, and the mass foams up. In a few minutes the reaction is over, and a thick green paste remains. Hot water (200 to 250 c.c.) is added, and after the chromium compounds have dissolved, the liquid is filtered. The red crystalline filter-cake is washed, then heated with 60 to 75 c.c. of 10 per cent. sodium carbonate solution to dissolve out naphthalic anhydride, and filtered again. The residue of crude acenaphthenequinone is boiled for a short time with 40 c.c. of 40 per cent. bisulphite solution,

then 75 c.c. of water added, boiled a little longer, and filtered hot.   The filtrate contains the bisulphite compound of acenaphthenequinone, which crystallises out partly on cooling.   The undissolved residue is extracted again with 20 to 25 c.c. of bisulphite solution.   The united filtrates are heated to boiling and excess of sulphuric acid added.   After boiling for some time, the acenaphthenequinone separates as fine yellow needles.   The yield is 40 to 41 per cent.   According to Graebe, even this 40 per cent. yield is only attained by adhering accurately to the specified conditions.

Another method of preparation, depending on the action of amyl nitrite and hydrochloric acid on acenaphthene, is patented by Kalle and Co. (G.PP. 228698, 233473; see also Reissert, *Ber.*, 1911, **44**, 1749).

Acenaphthenequinone is condensed with thioindoxyl and its derivatives to bright scarlet and red vat dyes of the type—
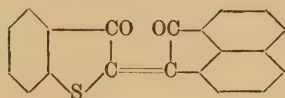
—known as Ciba Scarlet G, Ciba Red R, etc.

III. **Derivatives of Carbazole.**

Carbazole crystallises in colourless leaflets, m.p. 238°, b.p. 335°.   It is insoluble in water and sparingly soluble in most organic solvents.   100 parts of alcohol at 14° dissolve 0·92 part, and at the boiling-point 3·88 parts.   100 parts of toluene at 16·5° dissolve 0·55 part, and at 100° 5·46 parts.   It sublimes easily.   It is not appreciably basic in properties.

As already mentioned (p. 213), it occurs with anthracene in the solid which separates from anthracene oil, and is roughly separated from the anthracene by the pyridine treatment described.   The crude carbazole recovered from the pyridine solution is purified by heating with caustic potash at a high temperature (about 220° to 240°), when a potassium derivative is formed :
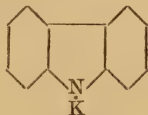
This is non-volatile, and any accompanying anthracene, phenanthrene, etc., can be distilled off under low pressure.   The residual potassium compound, on heating with water, is converted back into carbazole, which is then distilled for a final purification (G.P. 178764).

E.P. 139981 (Burt, Boulton, and Haywood, and F. D. Miles) describes a modifica-

tion of this method of purification. Crude carbazole is heated under pressure with an alkali metal, or oxide or hydroxide of the metal, in presence of an indifferent solvent, such as naphthalene or toluene, at a temperature below the melting-point of the carbazole-metal compound. The solvent is subsequently removed, and the carbazole-metal compound decomposed by boiling with water.

Carbazole itself is used in the preparation of Hydron Blue R, a vat dyestuff of unknown constitution. For this purpose, the carbazole is first condensed with *p*-nitrosophenol to form the indophenol :
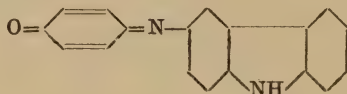
This indophenol is then converted into the dyestuff by heating with sodium polysulphide.

N-Ethylcarbazole—
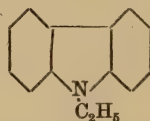
—is prepared by the action of ethylating agents—*e.g.*, ethyl chloride, on potassium-carbazole. It crystallises in leaflets, m.p. 67° to 68°, very soluble in ether and hot alcohol. It is used in making Hydron Blue G.

3 : 6-**Diaminocarbazole—**
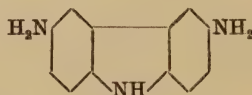
—crystallises in silvery leaflets (melting-point above 290°), sparingly soluble in hot water, alcohol, or benzene.

This is prepared by first nitrating carbazole to the dinitro derivative (G.P. 46438, Badische; G.P. 128853, Wirth), and then reducing this with sodium sulphide (G.P. 139568, Wirth).

It yields a tetrazo compound, and is used as a component in azo dyes, to which, like benzidine, it imparts the property of dyeing cotton without the aid of a mordant.

IV. Isoquinoline.

Crystallises in tables, m.p. 24°, b.p. 242° (760 mm.), D_4^{20} 1·0986. It has an odour like that of quinoline, and is volatile in steam. It is more basic than quinoline.

It occurs with quinoline and quinaldine in the heavy coal tar bases, and is most conveniently obtained from this source, although the separation is rather troublesome. A partial separation from quinoline and quinaldine can be accomplished by taking

advantage of the greater basicity of isoquinoline (G.P. 285666). But the main purification depends on the fact that the acid sulphates of quinoline and quinaldine are more soluble in alcohol than that of isoquinoline.

A method is described by Forsyth, Kelly, and Pyman (*J.C.S.*, 1925, **127,** 1661) as follows: Three gallons of "crude pyridine bases" (corresponding to 6 tons of coal tar) are dehydrated by shaking three times with aqueous sodium hydroxide (80° Tw.), and the product (10·85 litres) is distilled up to 170°, and then fractionated through a twelve-pear column. The various fractions, b.p. 200° to 280°, are fractionated similarly twice more, when 2·3 litres (2,470 g.) of heavy quinoline bases, b.p. 230° to 255°, are obtained. This fraction is converted into acid sulphate and crystallised fractionally from alcohol, when 185 g. of pure isoquinoline hydrogen sulphate, m.p. 207·5° (corr.), are obtained. This gives 102 g. of the base, b.p. 242° (corr.) over a range of 0·5°; m.p. 24° (corr.). The yield of isoquinoline from the heavy quinoline bases is thus about 4 per cent.

Another and more laborious method is given by Harris and Pope (*J.C.S.*, 1922, **121,** 1029).

Isoquinoline is used for the preparation of Quinoline Red.

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